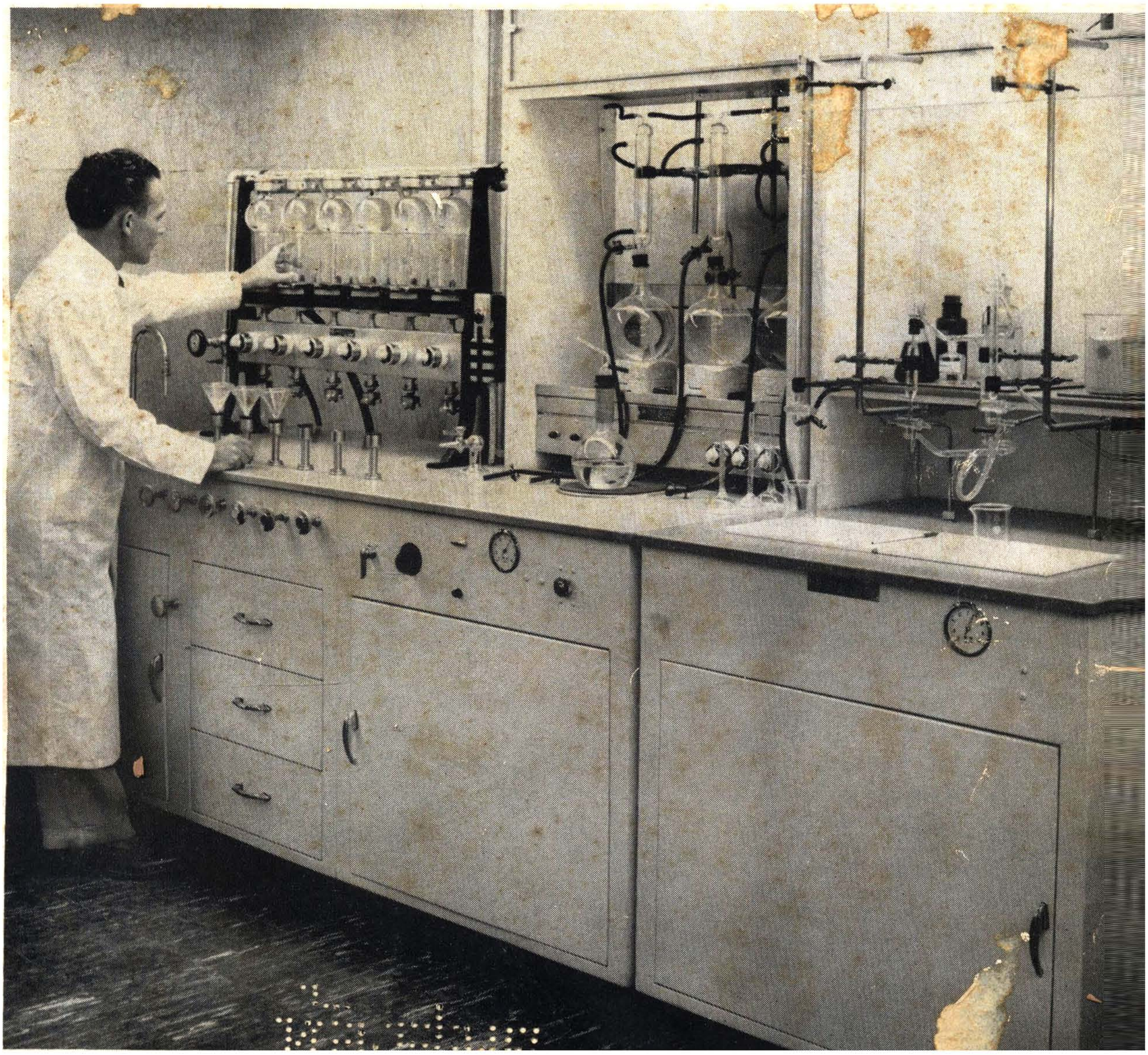
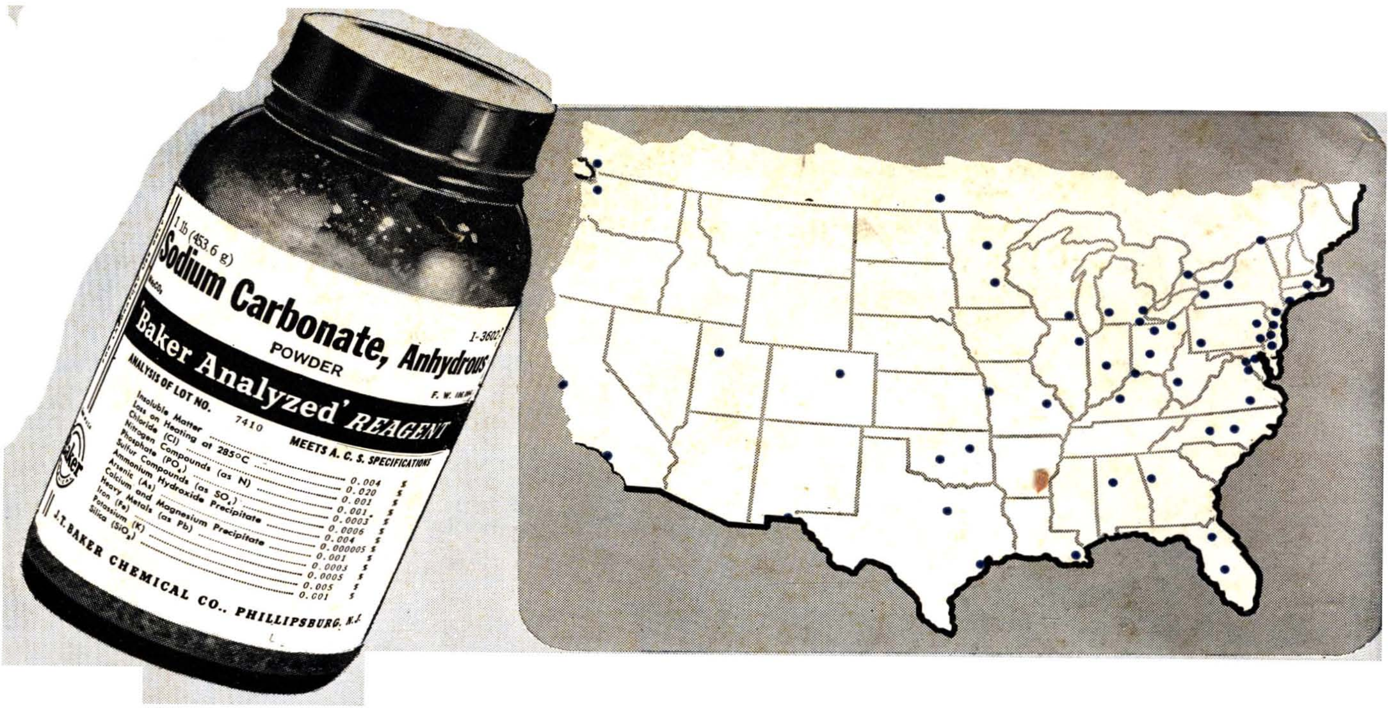
JANUARY 1954

ANALYTICAL CHEMISTRY



Laboratory of the Colorado Department of Agriculture at Denver designed and equipped for large volume of determinations. See pages 28A–29A


1 lb (453.6 g)
Sodium Carbonate, Anhydrous
POWDER
'Baker Analyzed' REAGENT
ANALYSIS OF LOT NO. 7410
MEETS A. C. S. SPECIFICATIONS
J. T. BAKER CHEMICAL CO., PHILLIPSBURG, N.J.

ANALYTICAL CHEMISTRY

Volume 26, No. 1 Issued January 23, 1954 Copyright 1954 by the American Chemical Society

SIXTH ANNUAL REVIEW OF ANALYTICAL CHEMISTRY

[END OF REVIEW SECTION]

(Continued on page 4 A)

This Month's Cover. One way to overcome the shortage of laboratory technicians and to free professionally trained chemists from housekeeping chores is to take advantage of the latest in laboratory apparatus, equipment, and furniture. This was the basic idea behind the laboratory of the Colorado Department of Agriculture. The photo shows the titration table and to the left, a crude fiber unit. Eight-foot table holds the 6-unit crude fiber condensers and all the equipment and services for this determination. Solutions are pressure delivered from cabinet storage. Filtrations are handled through a stainless steel vacuum manifold assembly and a system of maintaining hot solutions is a feature. For other pictures and story of lab, see pages 28 A–29 A.

CONTENTS, continued

CRYSTALLOGRAPHIC DATA

AIDS FOR THE ANALYST

The American Chemical Society assumes no responsibility for the statements and opinions advanced by contri tors to its publications. Views expressed in the editorials are those of the editors and do not necessarily repres the official position of the American Chemical Society. Published by the American Chemical Society, from 2 and Northampton Sts., Easton, Pa. Executive Offices, Editorial Headquarters, and Circulation Department, 11 Sixteenth St., N.W., Washington 6, D. C. Advertising Office: 330 West 42nd St., New York 36, N. Y. Brai Editorial Offices: Chicago 1, Ill., 86 East Randolph St.; Houston 2, Tex., 623 West Bldg.; New York 17, N. 60 East 42nd St.; San Francisco 4, Calif., 703 Mechanics' Institute Bldg.; London, Bush House, Aldwych. Ente as second-class matter at the Post Office at Easton, Pa., U.S.A., February 18, 1948, under the Act of March 3, 18 as 12 times a year monthly on the 15th. Acceptance for mailing at special rate of postage provided for in Sect 1103, Act of Oct. 3, 1917, authorized July 13, 1918. Annual subscriptions: members $3.50, nonmembers $4. Postage to countries not in the Pan-American Union $1.20. Canadian postage $0.35. Combination rate Analytical Chemistry and *Industrial and Engineering Chemistry:* members $7.00, nonmembers $8.00. Postage the combination: countries not in the Pan-American Union $3.90, Canadian postage $1.10. Single copies: curr issues, members $0.40, nonmembers $0.50; back numbers, prices on request, special rates to members. Claims missing numbers will not be allowed if received more than 60 days from date of mailing plus time normally requi for postal delivery of journal and claim. No claims allowed from subscribers in Central Europe, Asia, or the Pac Islands other than Hawaii, or because of failure to notify the Circulation Department of a change of address, because copy is "missing from files."

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The names of these new Emil Greiner flowmeters tell the whole story. We believe they are the most important development in flowmeters since the invention of the rotameter. Now you can obtain *complete predictability for all fluids!*

Heretofore you had to do individual calibrations for each specific fluid. With the Predictability Flowmeter, you can calculate the calibration curve *directly*, without the need of the experimental calibration that was necessary in the past.

An important feature of these flowmeters is a new teflon stop which provides quick interchangeability and ball replacement — at no extra cost!

predictability Flowmeters

PRINCIPLE OF OPERATION

The new predictability flowmeters consist of spherical floats in tri-flat tubes. These tubes are circular in cross-section at the bottom and triangular at the top. In between, the tube has a cross-section which progressively changes from a circle to an equilateral triangle whose sides are tangent to the circle. The balls which act as floats slide snugly in the tubes at all positions from top to bottom. As more fluid passes through the tube, the balls will rise and increase the annular area between the ball and the tube. The balls will come to equilibrium at a point where the weight of the ball is equal to the force required to flow the fluid through the annular area. This force which increases with flow also decreases as the annular area increases, thus permitting the ball to find an equilibrium position in the range of the instrument.

Because of the tri-flat construction, it is possible to obtain a generalized correlation of the flow of any fluid against the readings on the meter. This correlation depends upon plotting a flow coefficient against a viscous influence number for different positions on the tube corresponding to its readings. The only information required to obtain a calibration for a given fluid is the density and viscosity of the fluid under the conditions of flow.

The EMIL GREINER Co.
20-26 N. MOORE STREET E.G.Co. NEW YORK 13, N.Y.

or Complete Details
rite For Flowmeter Bulletin

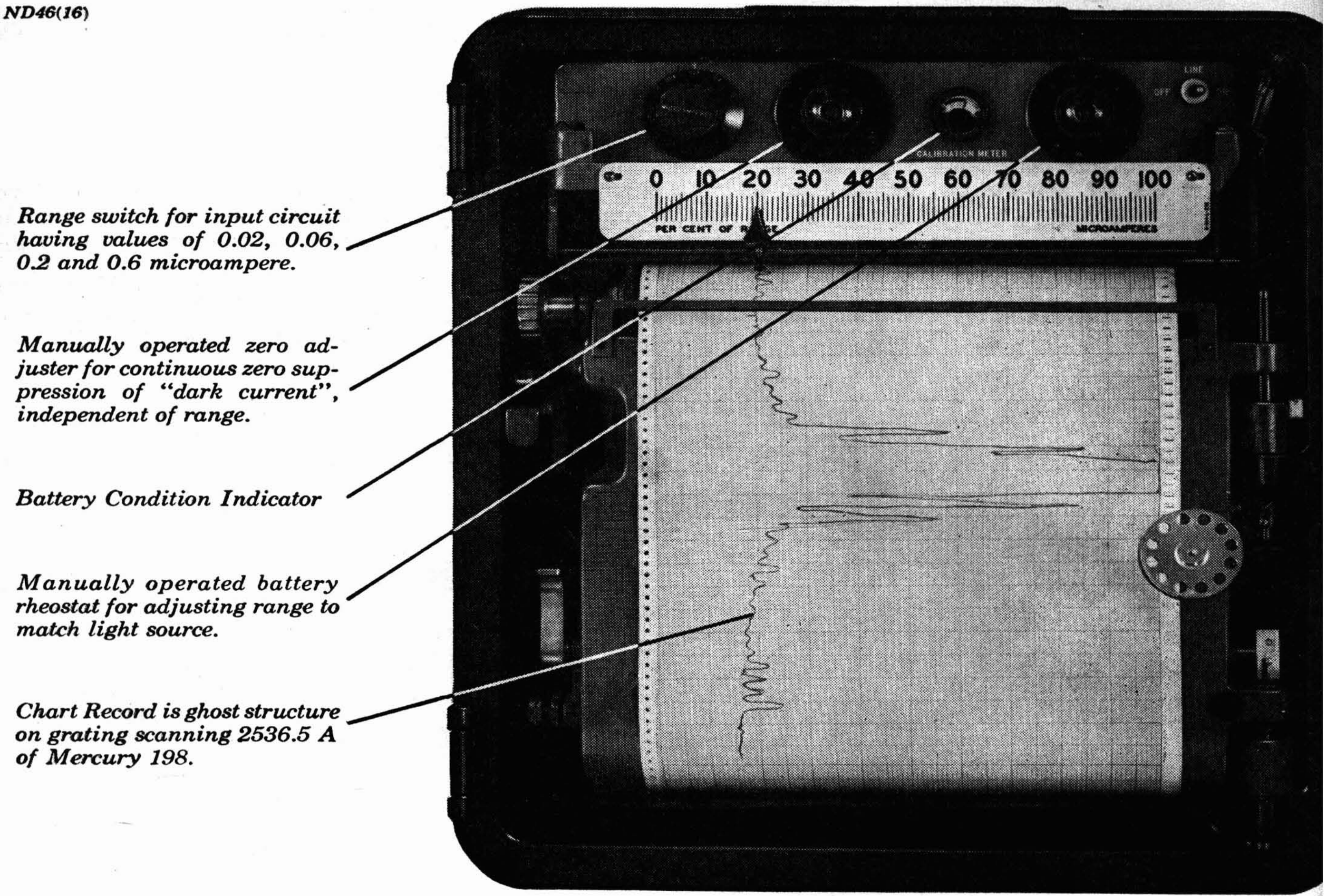
COMPLETE WITHOUT JOINTS		COMPLETE WITH JOINTS /1.		STANDARD TAPER JOINTS	NON-METAL FLOAT MATERIAL /2.	APPROXIMATE MAXIMUM READING IN ML./MIN. /3.	
CAT. NO.	PRICE	CAT. NO.	PRICE			Air	Water
G9142B	18.50	G9142C	22.25	10/30	Sapphire	80	1
G9143B	18.50	G9143C	22.25	10/30	Sapphire	400	10
G9144B	18.50	G9144C	22.50	12/30	Sapphire	2000	60
G9145B	18.50	G9145C	22.75	14/35	Glass	18000	550
G9148B	19.75	G9148C	24.25	19/38	Glass	68000	2000

NOTES

/1. Male inlet, Female outlet.

/2. Meters come with stn. steel and non-metal balls, may be used individually or combined.

/3. For stn. stl. ball. Approx. ½ for non-metal ball. Minimum reading approx. 1/10 of Maximum.


Range switch for input circuit having values of 0.02, 0.06, 0.2 and 0.6 microampere.
Manually operated zero adjuster for continuous zero suppression of "dark current", independent of range.
Battery Condition Indicator
Manually operated battery rheostat for adjusting range to match light source.
Chart Record is ghost structure on grating scanning 2536.5 A of Mercury 198.
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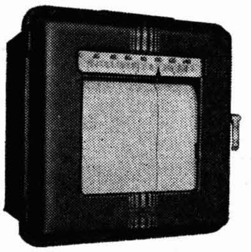
CALIBRATION METER
PER CENT OF RANGE
MICROAMPERES
LINE
OFF



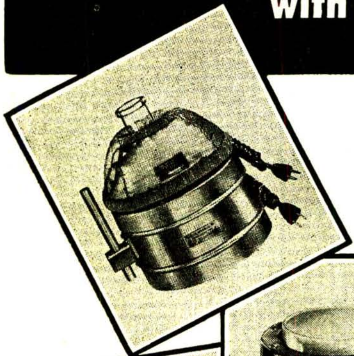
NOW — A *COMPLETE* LINE OF GLAS-COL HEATING MANTLES with ALUMINUM HOUSINGS!

TO INSURE longer mantle life, the entire Glas-Col Electric Heating Mantle line is now available, if desired, with attractive aluminum housings which feature built-in support clamps where needed. The aluminum housing protects the outside of the heater element without sacrificing the softness of the inner lining. It also protects the glass fabric from damage due to accidental boilover of chemicals . . . prevents the insulation from being disarranged with long use . . . and preserves its efficiency.

Glas-Col Mantles are a safe and economical means of heating various types of vessels commonly employed in chemical laboratories. Actual tests prove that the concealed wiring does not cause fire even when impregnated with inflammable fluids. Constructed of glass fabric, the mantles may be safely operated up to a maximum fabric temperature of 450° C. For applications requiring very high temperatures (to 700° C.), quartz fabric mantles with quartz wool insulation may be ordered.

Outstanding features include: (1) Safe, even heat distribution. (2) Exact heat input easily obtained. (3) Flask protected against breakage. (4) High thermal efficiency—over 80%. (5) Rugged construction.

Complete descriptive information and prices will be sent on request.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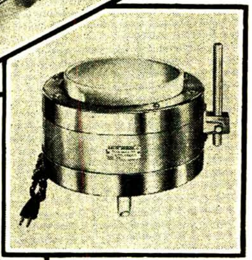
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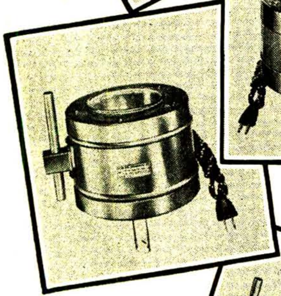
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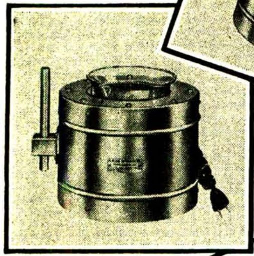
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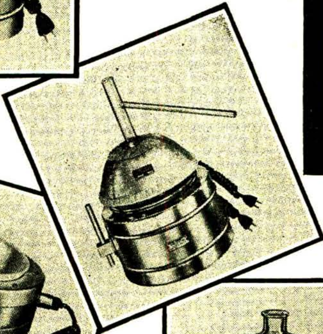
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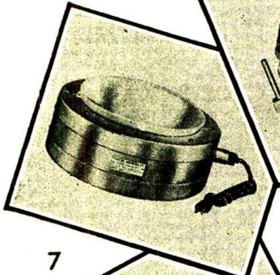
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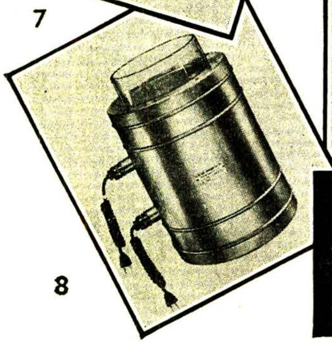
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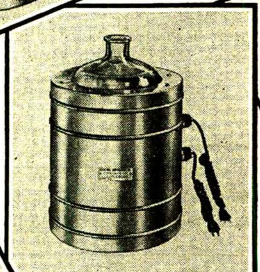
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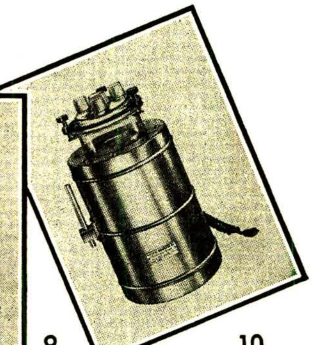
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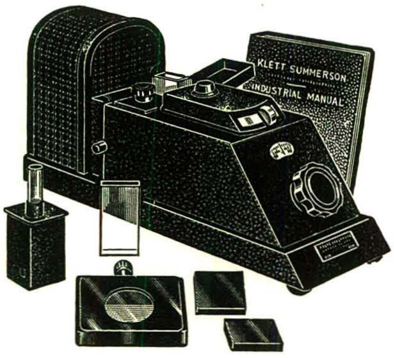
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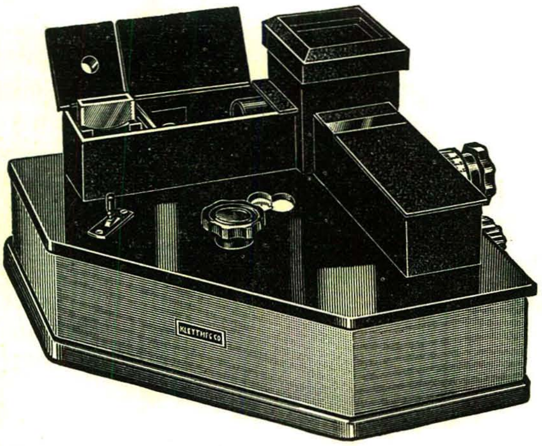
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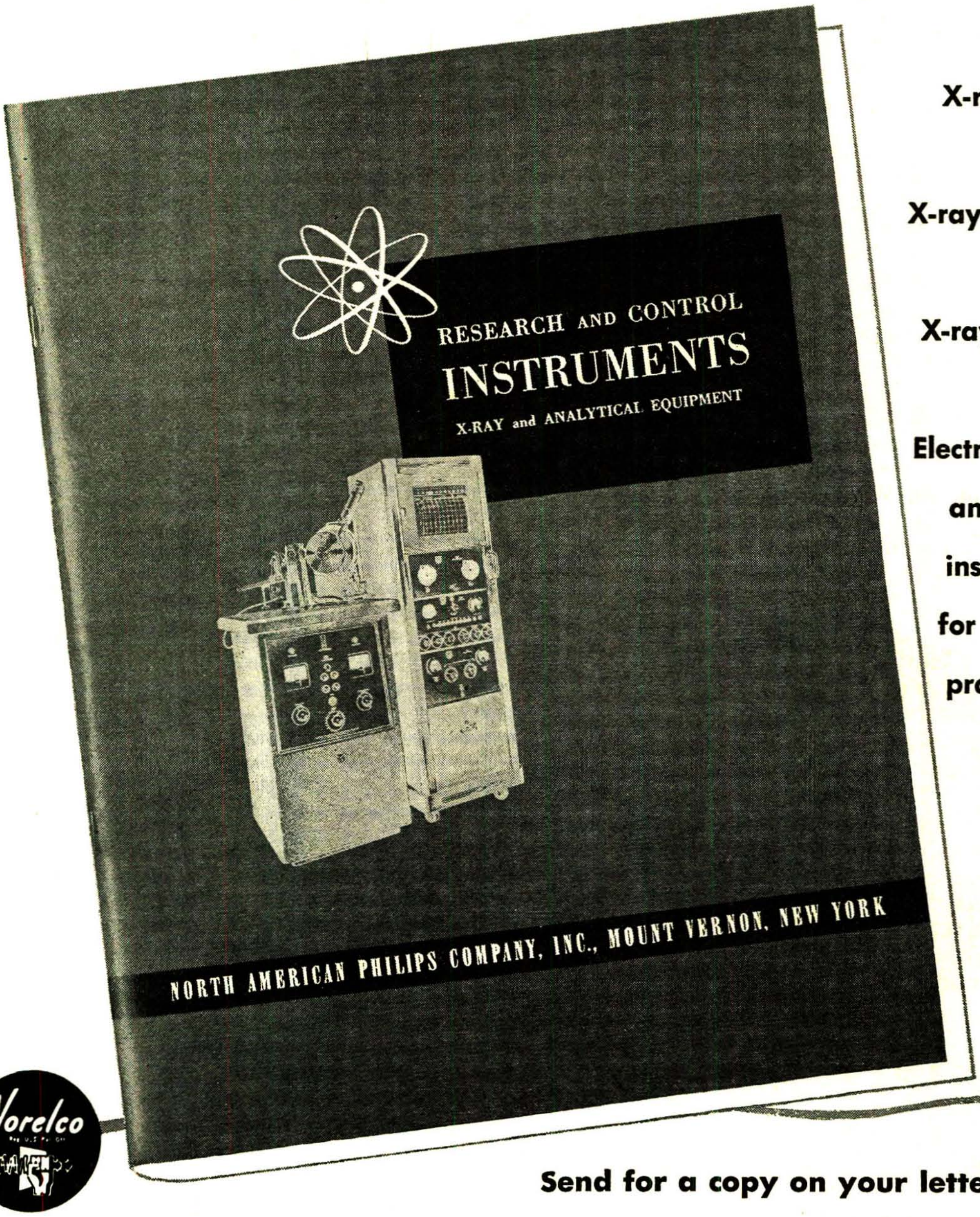



LA PINE
HIGH LEVEL DRAIN
STRAINER

Tales of the more than

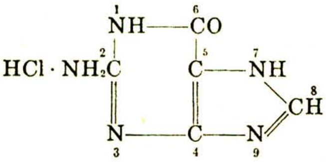
3500

EASTMAN ORGANIC CHEMICALS

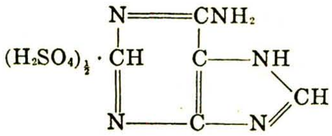
In Act IV, Scene 1 of *Macbeth* the weird sisters gather 'round the cauldron to work a reaction and catalog such items of medieval biochemistry as eye of newt and baboon's blood. Reminds us in a way of certain chemical spare parts of the life process to be found in various brown stock bottles in our own stockrooms.

For example, our various modifications of purine:

Guanine Hydrochloride (Eastman 1606), which takes its name from the Spanish word for the droppings of seafowl, crops up (without the convenient HCl handle, of course) in many situations where the substance of flora and fauna is chemically disassembled. We can obtain this 2-amino-6-oxypurine either from fish scales found at the bottoms of barrels that stand picturesquely on old New England wharves or as a by-product from the isolation of adenine. It is of some commercial importance as an ingredient of pearly lacquers.



Adenine itself we might obtain from glandular tissue or from tea, but we choose to make it from the nucleic acid in brewer's yeast. We sell it as *Adenine Sulfate* (Eastman 1645).

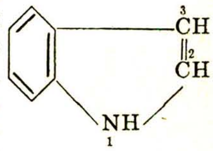


In nature the enzyme adenase deaminates adenine to 6-oxypurine and when this takes on water it becomes 2,6-dihydroxypurine, otherwise known as *Xanthine*, which is present in muscles, spleen, and urine and which we carry in highly purified crystalline form as Eastman 1644. One more oxygen in the 8 position of the purine structure gives *Uric Acid*, one of the principal constituents of kidney stones, available from us as purified crystals (Eastman 544).

When a pair of methyl groups attach themselves at the 3 and 7 positions of the xanthine molecule, it rises in the esthetic scale and becomes *Theobromine*. This contains no bromine, of course, but gets its name from a combination of Greek roots implying "food for the gods" because it is the principal alkaloid of chocolate. With us it's Eastman 1690.★

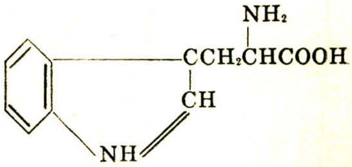
One more methyl group, attached at the 1 position through the metabolism of certain semi-tropical shrubbery, brings us to the beloved alkaloid *Caffeine* (Eastman 355)★ and the end of our present line of purines.

Or take our indoles:



Indole (Eastman 2773), the parent compound, is found in jasmine, orange blossoms, and feces. When a methyl group clings at the 3 position, you have *Skatole*, the most fundamentally unpleasant of all the stenches we keep in bottles. (As a precaution in case of accident, we have assigned *Skatole* to a chemist who happens to be olfactorily totally blind and deaf—a valuable man.) Despite its central role in scatology, *Skatole* is also a fixative in fine perfumery. Where in the misty seas between psychophysics and psychoanalysis lies the explanation of this dichotomy, we know not.

Both indole and skatole are breakdown products of the essential amino acid L-(-)-*Tryptophane*. This, too, we stock as Eastman 2025. (At less than half the price we can also supply DL-*Tryptophane* (Eastman 5578).)



One aspect of indole chemistry that would surely have interested the sisters is represented by *3-Indoleacetic Acid* (Eastman 4271), *3-Indolepropionic Acid* (Eastman 2530), and *3-Indolebutyric Acid* (Eastman 4275)—auxins all. They would have enjoyed using them to confound a bean sprout trying to get itself properly pointed between light and darkness. Whether they would have had similar interest in *1,3-Dimethylindole* (Eastman 5331) and *3-(2-Aminoethyl)indole Hydrochloride* (Eastman 2954) is open to speculation.

Whether or not these purified purines and indoles can serve your purposes as analytical standards or as weapons for deep probing into the nature of life, there are more than 3500 other compounds you can order from the catalog of Eastman Organic Chemicals. If you haven't a copy, write *Distillation Products Industries*, Eastman Organic Chemicals Department, Rochester 3, N. Y.

★Though *Theobromine* and *Caffeine* have pharmaceutical uses (as diuretics, among other applications), we sell them for chemical purposes exclusively and only on written assurance that they will not be used or resold as drugs or food.

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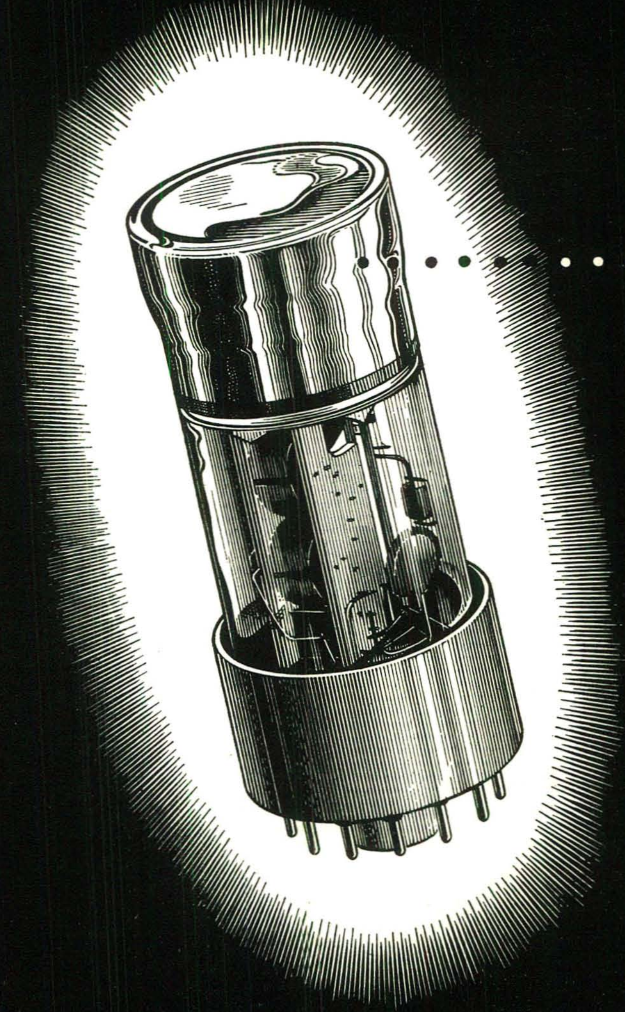

THE ANALYST'S COLUMN

L. T. HALLETT, Science Editor

The Annual Priestley Lectures, started in 1927, have largely dealt with physical topics, and the one given last year by James J. Lingane of Harvard continued the subject but as applied to analytical chemistry. His lectures, "Innovations in Electroanalytical Chemistry," traced the beginnings when in 1801 W. Cruikshank first observed the electrolytic deposition of silver and copper, and suggested electrolysis as a means of qualitatively detecting these elements.

Electrogravimetric analysis stems from the investigations of O. Wolcott Gibbs at Harvard when he disclosed in a paper published in 1864 in *Zeitschrift für analytischen Chemie* that copper could be determined quantitatively by deposition onto a tared platinum cathode. Later Henry J. S. Sand in England in 1906 pioneered in controlling the potential of the cathode so that only the desired metal is deposited, which modern instrumentation has made automatic instead of manual.

Potentiometric and conductometric methods in locating equivalence points were pioneered by the fundamental work of Poggendorf, who invented the potentiometer in 1841, and Wheatstone in his development of the balanced bridge technique for measuring electric resistance.

Professor Lingane's lectures finally dealt in some detail with the newer developments in this field, such as oscillometric titrations by Jensen and Parrack, polarographic techniques invented by Heyrovský and Shikata in 1925, and coulometric analysis developed by Szebelledy and Somogyi in 1938. Finally, the subject of electrographic analysis and electro spot testing was dis-

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This cathetometer is intended for measurements and observations in both industrial and educational laboratories wherever an inexpensive instrument of good precision is needed. It is rigidly constructed and every essential adjustment can be made simply and positively.

The telescope is mounted horizontally on a carriage which may be moved up or down or around the 30-mm vertical rod. A tangent-screw adjustment permits precise leveling and a sensitive elevation adjustment is incorporated in the carriage. An auxiliary level in the base greatly accelerates the leveling process. Magnification is 12x at 45 cm.

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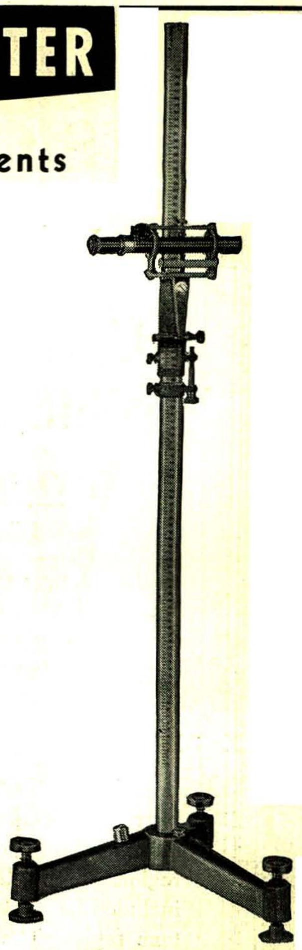

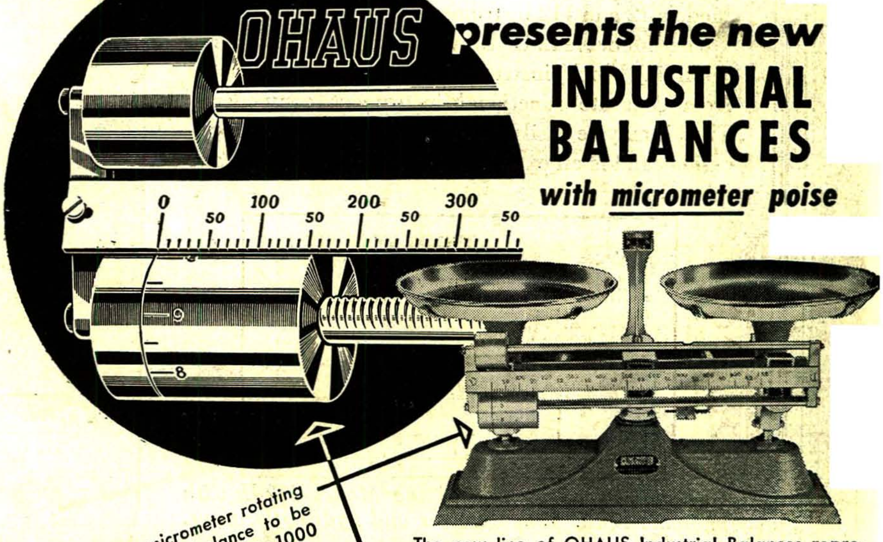

OHAUS presents the new INDUSTRIAL BALANCES with micrometer poise

This new type micrometer rotating poise enables this balance to be used for a range from 0.5 to 1000 gram without additional weights. The poise is designed so that it may be slid along the beam for rapid traverse and rotated for final positioning.

The new line of OHAUS Industrial Balances represents the very latest in engineering design and material. These balances are equipped with light weight, high strength duralumin beams, self-aligning polished agate bearings, precision hollow-ground tool steel knife edges, and many other exclusive OHAUS features. Other models are available with stainless steel plates, polished brass scoops or with beams calibrated for combination metric and avoirdupois weighings.

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SCALE CORPORATION
1050 COMMERCE AVE.
UNION, NEW JERSEY

facts on Infrared *for the laboratory*

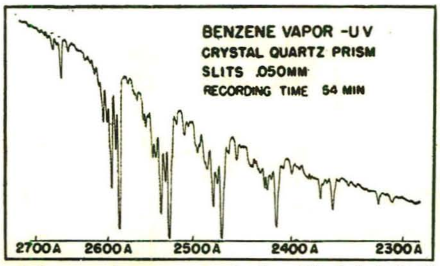
How to record UV, visible, and IR spectra on *one* instrument!

Though infrared analysis is basically the more powerful analytical tool, there are many problems that are more conveniently handled by ultraviolet analysis. Accordingly, it is convenient to have an instrument available that may be used in either region as the occasion arises.

Such an instrument is the Perkin-Elmer Model 112-U Universal Spectrometer. Though basically a single beam, double pass infrared spectrometer, the instrument is equipped with all necessary accessories for recording spectra in the ultraviolet and visible regions as well. In addition, a lead sulfide detector is included for work in the increasingly important overtone region. The spectrum reproduced here shows typical performance in the ultraviolet regions.

The UV and near infrared components used on the Model 112-U may be added to existing Perkin-Elmer Models 12 and 112 instruments.

The Model 112-U Universal Spectrometer is a "Building Block" instrument—that is, it is constructed from separate functional instrument components. Thus it may be easily modified to meet special applications and is an extremely valuable addition to any laboratory.



Ultraviolet performance of the Model 112-U with photomultiplier tube detector and hydrogen source.

The Perkin-Elmer Corporation, 860 Main Avenue, Norwalk, Conn.
Southern Regional Office: New Orleans, Louisiana

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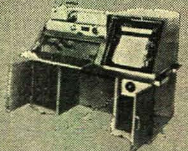
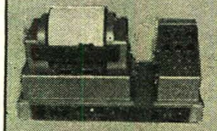
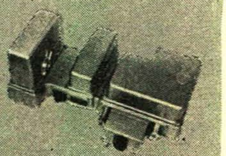
The ONLY complete range of infrared instruments and accessories to meet all research needs!



Model 112 Double Pass Infrared Spectrometer—single beam, high resolving power, excellent for structural analysis. Suitable attachments for all spectral ranges. *Write for Bulletin 102.*



Model 21 Double Beam Infrared Spectrophotometer—The fastest and most efficient instrument commercially available for the recording of large numbers of spectra. Records directly in percent transmission. *Write for Bulletin 104.*



Model 13 Ratio Recording Infrared Spectrophotometer—Records double or single beam with many features of both the Model 112 and 21. Ideal for the small laboratory with a wide variety of problems. *Write for Bulletin 110.*

ACCESSORIES:

Demountable Cell—may be assembled to any thickness—for liquids, capillary films, mulls of solids—and films and powders.

Fixed Thickness Liquid Cell—for nearly all liquids and solution work. Standard thickness between 0.025 and 1 mm—others to order.

Standard Gas Cells—2, 5, 10 cm and 1 and 10 m path lengths for various absorption studies.

Microcell—obtains good spectra with 25-100 micrograms—available in thicknesses from 0.025 to 3 mm.

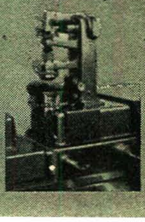
Variable Space Liquid Cell—has accurately variable path length of 0 to 5 mm to bring out features of a spectrum and to compensate for solute absorption in double beam spectrometry.

Reflectance Attachment—for specular reflectance studies of solid materials.

Pressure Cells—for liquids or gasses; path lengths from 0.025 to 50 mm, pressures up to 300 psi. Useful in trace absorption or overtone work. Long and short sizes.

Heating Stage and Heating Stage Power Supply—used with above attachment; permits heating to about 300° C. For studying polymerizations and oxidations. Cycling feature of the Model 21 automatically records reaction stages taking place.

Polarizer—for studies of crystal and molecular orientations. Rotable Cell—To assist in sample orientation for polymerization studies.



Microscope—For analysis of samples of few microns in size as single fibers, tissues, crystals, etc.

Write for Product Bulletin A-3 for more information about these accessories.

ANALYST'S COLUMN

cussed. This work stems largely from the investigations in 1929 of Fritz and Glazunov.

Copies of these lectures may be purchased for $2.00 from the honorary chemical society of Phi Lambda Upsilon, Pennsylvania State University, State College, Pa.

The short history given in the foreword is rather interesting:

> Joseph Priestley, theologian, philosopher, and scientist, was born in England on April 13, 1733. He was ordained as a Presbyterian minister, but later rejected Calvanism and adopted Unitarian views. He studied chemistry and electricity at Warrington Academy. He was given an honorary LL.D. by Edinburgh University in 1764 and became a Fellow of the Royal Society in 1766. In 1774 his chemical experiments produced "dephlogisticated air," which Lavoisier named oxygen. Priestley's openly expressed sympathy with the aims of the French Revolution led, in 1791, to the wrecking of his home and the destruction of his library and scientific apparatus. In 1794 he emigrated to America and settled in Northumberland, Pa., where he built a home on the banks of the Susquehanna River. Here he continued his writing and chemical experimentation until his death in 1804.
>
> In 1919, the alumni of the Chemistry Department of the Pennsylvania State College purchased the Priestley residence at Northumberland. Near the house a museum was built to preserve such relics of Joseph Priestley as could be obtained, and then the property was deeded to the college to assure permanent maintenance of this memorial. Since the Priestley home is about seventy miles from State College, it was felt that the establishment of a less remote memorial would be desirable. Wheeler P. Davey, research professor of chemistry and physics, suggested the establishment of a series of lectures marking the anniversary of Priestley's birth.
>
> In April 1927, the Priestley Lectures were inaugurated at the Pennsylvania State College under the sponsorship of Dr. Davey and other members of the faculty of the Department of Chemistry. In 1931, Mu chapter of Phi Lambda Upsilon, honorary chemical society, assumed the financial responsibility for the lecture series under cosponsorship with the Departments of Chemistry and Chemical Engineering.
>
> The original concept for the Priestley Lecture Series was threefold in nature: (1) to establish a living memorial for Joseph Priestley; (2) to honor a succession of contemporary American scientists; and (3) to demonstrate that theoretical chemistry was a vital functional part of modern applied chemistry.

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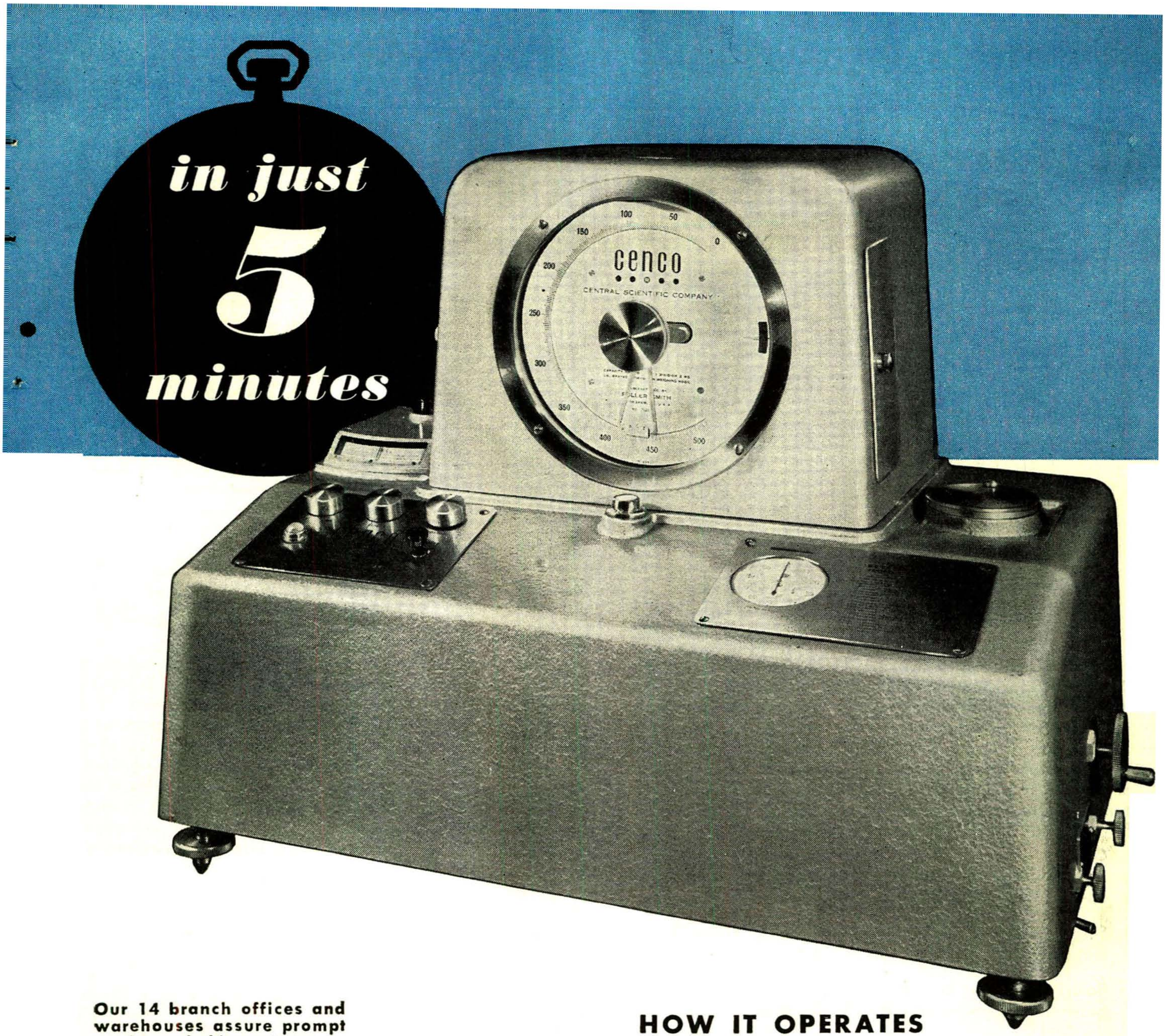

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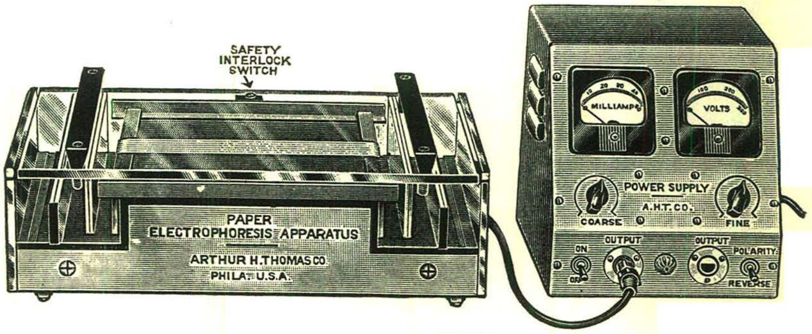

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ANALYTICAL CHEMISTRY

WALTER J. MURPHY, Editor

Salute to USP and NF

On the bookshelves of analytical chemists in the pharmaceutical industry, the most dog-eared reference works are likely to include the United States Pharmacopeia and the National Formulary. For decades, both of these volumes have been indispensable guides to standards of strength, quality, purity, and identity of hundreds of drugs widely used throughout the United States. In fact, so valuable and authoritative are these standards that they also serve as drug specifications in many countries abroad. Thanks to the work of USP and NF, the public is given ample assurance that approved drugs are not only safe but also useful agents for the treatment or cure of human ills.

Our appreciation of the work of USP and NF was further heightened recently at a meeting of the Analytical Group of the American Chemical Society's North Jersey Section. Those attending had the opportunity to hear from two foremost leaders in this field, Lloyd C. Miller, director of pharmacopoeial revision of the United States Pharmacopeia, and Justin L. Powers, chairman of the Committee on National Formulary of the American Pharmaceutical Association. Their discussion of the work of USP and NF left no doubt whatever that these two compendia are not only of immense service to the physicians, pharmacists, clinicians, and drug manufacturers of the nation but also—and quite importantly—to the analytical chemists.

Although both USP and NF serve the same function of establishing drug standards, each operates within its own sphere. There is no overlapping. In general, drugs described in USP are those considered the most effective forms of medical treatment. On the other hand, those described in NF are drugs which, although they may have long been widely used, are not considered the very best available today. Of course, NF is not merely a catchall for outmoded drugs. Where a product has only very limited value or no value whatever, it is covered neither in USP nor in NF.

The U. S. Pharmacopeia and the National Formulary both have had long and distinguished histories. The older of the two is USP, which first appeared in 1820, even though the sponsoring agency, the U. S. Pharmacopoeial Convention, was not formally incorporated until 1900. The National Formulary, sponsored by the American Pharmaceutical Association, was first issued in 1888. Although both were published once every 10 years until 1940, they are now issued once every 5 years.

USP was founded by a group of physicians who felt an acute need for reliable drug standards. Lack of drug uniformity was one of the bugbears of the day. Those were the times when doctors, lacking many of the conveniences of the present, were obliged to roll their own pills and perform other functions that, in later years, were turned over to the pharmacists. Likewise, responsibility for the preparation of USP gradually passed from the physicians to leaders among the nation's pharmaceutical chemists, to the extent that their aid and advice today are clearly indispensable.

The drug standards of USP and NF achieved a rapid rise in status at the turn of the century, when they were adopted as official in many state laws controlling the practice of pharmacy and the quality of foods and drugs. The Federal Food and Drug Law of 1906 required that all drugs listed in USP or NF comply with the standards set up by these two compendia. The Federal Food, Drug, and Cosmetic Act of 1938 defines the term "drug" as a product recognized by either USP or NF.

In both compendia, the official specifications for physical chemical tests and the assay of drug potency are critical and specific. The assay not only indicates the percentage of the actual drug but furnishes added assurance of its quality, purity, and identity. Ordinarily, the analytical procedure involves either the isolation of the active principle of the drug or its identification by an entirely characteristic chemical reaction. Where two or more methods of equal precision or specificity are available, the simplest procedure is adopted.

Virtually every principle of analytical chemistry is used in the official assay of drugs. In recent years, increasing emphasis has been placed on instrumentation and spectrophotometric techniques. In the forthcoming revisions of USP and NF, use will be made for the first time of analyses involving titrations in nonaqueous media.

Even with the best chemical methods available, difficulties are frequently encountered in the interpretation of end points. As a partial answer to the problem, USP and NF provide high-purity reference standards that may be assayed in parallel with the drug under test. USP alone furnishes more than 50 such reference standards.

The accuracy and sensitivity of official procedures are, of course, dependent on the purity of the reagents used. Thus, both USP and NF have issued standards for reagent chemicals. Wherever possible, these standards are identical or at least very similar to those established by the American Chemical Society.

The creation of drug standards is a tremendous cooperative undertaking, enlisting the efforts of hundreds of technical specialists. Before a set of specifications is issued, it is critically reviewed in numerous scientific laboratories and colleges of pharmacy throughout the nation. At all times, these standards are arrived at democratically by processes of trial and criticism.

The target date for the publication of the latest revisions of USP and NF is January 1955. We look forward with keen interest to the release of these newest compendia, which unquestionably will match if not exceed the high standards of the past.

6th Annual Review of ANALYTICAL CHEMISTRY

FOR THE SIXTH TIME a group of outstanding analysts have prepared reviews of recent developments in the various fields of analytical chemistry. The articles covering the theoretical or fundamental material appear on the following pages. In January 1953 eleven articles reviewed the applications of new developments in a number of industries and fields of specialization.

As in previous years, these review articles will be combined in a single reprint for those who require it as a ready reference. Copies will be available at $1.50 each from the Reprint Department, American Chemical Society.

—The Editors

Light Absorption Spectrometry

M. G. MELLON
Purdue University, Lafayette, Ind.

IF ONE may judge by the number of publications in the field of light absorption spectrometry during the past 2 years, the popularity of such methods is still increasing. One evidence of this is a count of such articles (*312*) appearing in ANALYTICAL CHEMISTRY during 1950–51, as compared with those published in the same periodical during 1929–30.

Because the relevant literature is too extensive to make a total report possible, selections were made of what seem representative examples of the different subjects treated. This survey covers the literature approximately to August 1953. In general, the previously used outline has been followed. The chemistry of preparing a system for measurement comes first. This is followed by instruments and measurement; then come applications to specific situations.

CHEMISTRY

The word "chemistry" is employed to include all kinds of separative processes and preparative transformations required to render the sample system amenable to absorptiometric measurement. In this discussion, as in previous reviews, consideration is limited to those aspects of the subject which concern the production of satisfactory absorbing species and to their nature.

Nature of Absorbing Systems. Some widely used color-forming processes, still of unknown mechanism, show that one does not have to understand their nature in order to apply them. If possible, however, a real analyst much prefers to know what happens and how the process works. Such knowledge may well guide more effective specific applications.

Increasing study is being given to such systems, with perhaps most attention being directed to metal-chelate compounds (*302*). Herniter (*204*) reviewed the determination of the formula of complex ions by spectrophotometric methods, and Milazzo (*315*) discussed more broadly the relation of absorption spectra to chemical reactivity. Charlot and Gauguin's book (*90*) is the best resume of methods for investigating the nature of reactions in solution.

Continued interest is shown in the century-old iron(III)–thiocyanate reaction. Although Mitchell and Macdonald (*324*) found only the monomer of ferric thiocyanate in ether and alcohol, partition experiments of Macdonald *et al.* (*290*) indicate that all of the complexes from $FeSCN^{++}$ to $Fe(SCN)_6^{---}$ occur. Babko and Kodenskaya (*20*) decided that $Fe(SCN)_4^-$ can be extracted best in various organic solvents. Melnick *et al.* (*313*) found that the smallest ratio of thiocyanate to iron which can give highest extraction is between 4 and 5 to 1 for butyl phosphate. Other thiocyanate complexes included cobalt(II) (*19, 389, 405, 406*), chromium(III), (*249*) and vanadium(III) and (IV) (*159*).

Chloride complexes of metals included iron(III) (*157*), cobalt(II) (*116*), and eight of the heavy metals (*121*). Of similar nature is the work on the monobromo complex of copper(II)(*144*).

Interesting redox studies are the reduction of permanganate with oxalate (*296*), the oxidation of manganese(II) with periodate (*472*), and the complexing of titanium with hydrogen peroxide (*21*).

The color of gold hydrosols was studied by de Brouckère *et al.* (*64*) and the preparation and use of tellurium hydrosols by Johnson *et al.* (*225, 226*). An extensive study concerns, among other items, various inorganic and organic complexes of vanadium(IV) and (V) (*132*).

Heteropoly systems maintain their share of attention. Strickland (*439*) prepared and studied the usual α-molybdosilicic acid and a new β-molybdosilicic acid. Bacon (*24*) also studied molybdosilicic acid and its reduction with ferrous sulfate. Ripan and Liteanu attribute certain results with phosphoric acid (*379*) and boric acid (*380*) to the respective Rosenheim hypothetical acids, $H_7(PO_6)$ and $H_9(BO_6)$. Souchay and Faucherre (*426*) studied extensively the constitution of molybdophosphate solutions; Burstein (*71*) studied their reduction with conjugated substances and Ferrari (*147*) with various other reagents. Milletti (*318*) found that the absorbances of molybdophosphate, arsenate, and silicate varied with time of formation of the complexes.

These studies are mainly concerned with the use of inorganic substances as color-forming reagents. Probably a larger number deal with the use of organic substances, especially those forming chelate-type complexes with metal ions. Freiser *et al.* (*154*) applied the Calvin-Bjerrum method to determine the chelate stability of nine metals, and later Johnston and Freiser (*227*) investigated the stability of 8-quinolinol with 10 metals. Phillips and Price (*359*) compared some of the same systems with those using 8-hydroxyquinaldine. Systematic studies (*85*) of metal chelates are under way.

The characteristics of the lead dithizone system were treated mathematically by Milkey (*316*). Cooper and Sullivan studied critically the use of this reagent for determining lead, mercury(II), silver, and zinc (*101*).

Studies of cyclic nitrogen reactants include the configuration of 2,2′-bipyridine (*148*), ferrous complexes of the 5-methyl, 5-phenyl, 5-chloro, and 5-nitro derivatives (*58*) and the 4- and 4,7-[(dialkylamino)alkylamino] derivatives of 1,10-phenanthroline (*475*), and copper complexes with 28 mono-, di-, tri-, and tetramethyl-1,10-phenanthrolines (*289*).

Study of the old iron-phenol system (*27*) led to the formula $Fe[Fe(OPh)_6]_3$. Similar studies dealt with the composition of positively charged complexes of iron(III) with phenols and enols (*65*), and with complexes of several metals with 2-aminophenol and 2-aminobenzenethiol (*88*). Complexes of several amino acids with copper (*107, 133, 325*) and with silver (*326*) have been studied. Monk also considered the tendency of such complexes to form.

A number of unrelated papers deal with individual organic compounds. Included are salicylaldehyde for several colorless cations (*52*); β-diketones for copper (*299*); α-diimines for iron(II) (*259*); sulfosalicylic acid for aluminum and nickel (*271*); ethylenediaminetetraacetic acid for seven lanthanon metals (*468*); chloranilic acid for zinc (*447*); nitroso R salt (*70*) and 1-nitroso-2-naphthol (*337*) for cobalt; nitroso R salt for iron(II) (*117*); thymol for titanium (*180*); 2,4-pentanedione for manganese(III) (*79*); 4,5-dihydroxy-2,7-naphthalenedisulfonic acid (chromotropic acid) for titanium (*59*); alizarin for six metals (*129*); four reagents for iron (*425*); several reagents for ruthenium (*479*); and triphenylarsonium thiocyanate for iron (*135*).

Few papers of this nature were noted dealing with organic systems. Kiss attempted to classify solvents on the basis of their influence on the absorbance curves of organic compounds (*250*).

Specific Methods. In the previous section the interest centered in the nature of the color-forming reactions—that is, what the process is, how it proceeds, the identity of the absorbing species, and the variable factors involved. Many more studies deal rather specifically with methods from the viewpoint of finding a workable reaction. The principal objective in these investigations was to find methods which are better in some way. Such methods are included in this section, arranged on the basis of the kinds of substances involved. No effort has been made to segregate all the new methods, as many abstractors and often even authors themselves are not clear on this point.

INORGANIC CONSTITUENTS. Methods for a number of constituents employ a variety of reagents, chiefly inorganic. Examples are several reagents each for bromide (*53*), iodide (*54*), and chloride (*55*); sols of the sulfides of berylium, copper, palladium, and silver (*454*); a mixture of four compounds for silver (*388*); thiocyanate for niobium (*156, 272*), for molybdenum (*275*), and for uranium (*106*); hydrogen peroxide for niobium and tantalum (*91*); hypochlorite for ruthenium (*18*); sulfuric acid for uranium and chromotropic acid for titanium (*419*); copper uranyl acetate (*356*) and nickel uranyl acetate (*412*) for sodium indirectly; Nessler's reagent for ammonia (*416*); and the fading of iron(III) thiocyanate for mercury(II) (*66*).

Studies continue on the use of heteropoly complexes as a means for determining various constituents. Examples are molybdenum blue for silicon (*321*), germanium (*139*), arsenic (*30, 241*), and phosphorus (*160, 216, 236, 335, 382*). In these methods, various reductants are recommended.

Other investigators used the heteropoly acids without reduction. In the presence of phosphate silicon is determined as molybdosilicic acid, following extraction of the molybdophosphoric acid with butyl acetate (*237*). Gericke and Kurmies (*168*) used the mixed molybdovanadophosphoric acid for phosphorus, while Murakami (*329*) determined vanadium as tungstovanadophosphoric acid. One study considered the forms of silicate susceptible to colorimetric determination (*93*). Two indirect methods employed molybdophosphoric acid for palladium (*286*) and for zirconium (*244*).

In many methods an organic substance is the principal reactant giving the colored system with the desired inorganic constituent. New methods of this type are illustrated by the following examples: copper with 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (*422*) and with 2,9-dimethyl-1,10-phenanthroline (*421*); zinc with *o*-[α-(2-hydroxy-5-sulfenylazo)benzylidenehydrazino]benzoic acid (*480*); molybdenum(VI) with disodium 1,2-dihydroxy-3,5-benzenedisulfonate (*481*); cerium(III) with Sunchromine Pure Blue B (*323*); uranium with 2,4-dihydroxyacetophenone oxime (resacetophenone oxime) (*463*); cobalt with *o*-(mercaptoacetamido)-*p*-nitrophenol (*72*); and calcium separated as oxalate with diphenylamine and phosphoric acid (*351*).

Other methods of this general kind are iron(III) with 3,5-dinitrosalicylic acid (*165*), with protocatechualdehyde (*410*), with thiogallic acid (*238*), with triphenylmethylarsonium chloride and ammonium thiocyanate (*134*), and a number of cyclic nitrogen compounds, the best being 3,5,6,8-tetramethyl-1,10-phenanthroline (*212*); iron(II) with 2-picolinic acid (*294*); copper with diethyldithiocarbamate (*403*), with phenylsemicarbazide (*118*), and with the methyl ether of 2-isatoxime (*127*); nickel with 1,2-cycloheptanedionedioxime (*146*); cobalt with sodium diethyldithiocarbamate (*368*); mixtures of cobalt, copper, and nickel with tartrates (*51*); copper, gold, mercury, palladium, or silver with *p,p*′-bis(dimethylamino)thiobenzophenone (*166*); titanium with 8-quinolinol (*162*) and with chromotropic acid (*349*); germanium with quinalizarin (*334*) and with phenylfluorone (*98*); niobium with pyrogallol and tantalum with sulfuric acid (*177*), and the same metals with pyrocatechol (*451*); ruthenium with thiourea (*333*) and with *p*-nitrosodimethylaniline (*108*); magnesium with Eriochrome Black T (*193*) and with titanium yellow (*170*); silver with *p*-dimethylaminobenzalrhodanine (*82*) and with 5-(*p*-diethylaminobenzylidene)-rhodanine (*394*); cadmium with a refined dithizone method (*391*), tin with dithiol (*242*); rhenium with three dioximes (*358*); bismuth with dithiocarbamidohydrazine (*185*); zirconium with oxalohydroxamic acid (*123*); calcium indirectly with oxalohydroxamic acid and iron(III) (*124*); molybdenum, uranium, and vanadium with salicylhydroxamic acid (*46*); and antimony with methyl violet (*178*).

For the alkalies one finds the determination of lithium with 1-(*o*-arsonophenylazo)-2-hydroxy-3,6-naphthalenedisulfonic acid (*338*); potassium with dipicrylamine (*395*); and cesium, potassium, and rubidium with dipicrylamine (*396*).

Various methods illustrate the determination of nonmetal constituents. Examples are hydrazine with picryl chloride (*265*) and with *p*-dimethylaminobenzaldehyde (*473*); carbon, as carbon dioxide, with alizarin yellow R in sodium hydroxide (*138*); fluoride through bleaching of the thorium-thoron complex (*211*), and through the prevention of full color development of the thorium–chrome Azurol S lake (*377*); cyanate with a pyridine–cupric nitrate reagent (*304*); and chromate with benzidine (*152*).

Organic Substances. If the environment is favorable, some organic compounds are sufficiently colored to make direct measurement feasible. An example is vitamin B_{12}, following separation of the interferences (*301*), or hydrolysis to give a red acid for measurement (*200*); the acid may be esterified with octyl or heptyl alcohol.

Reaction with another organic compound to form a color or to enhance or change a color of low intensity is common. Examples are the determination of formaldehyde with Denigès hydrostrichnic reagent (*80*) or by the formation of diacetyldihydrolutidine (*336*); 2,8-diaminoacridines coupled with resorcinol (*122*); acetone, and through it isopropyl alcohol and propylene, condensed with furfural (*141*); indole with the xanthydrol reaction (*145*); thiophen with alloxan and isatin reagents (*155*); 2-(*p*-*tert*-butylphenoxy)isopropyl-2-hexachloride, following dechlorination and nitration, with methyl ethyl ketone (*398*); proflavine with *N*-(1-naphthyl)ethylenediamine (*411*); amino acids with ninhydrin (*420*); desoxycholic acid with salicylaldehyde (*444*); lactic acid, via acetaldehyde, with *p*-hydroxybibenzene (*456*); trichloroacetic acid, via chloroform, by Cole's method using carefully controlled conditions (*319*); *N*-trichloromethylthiotetrahydrophthalimide with dihydroxybenzene (*251*); 2- and 3-*tert*-butyl-4-hydroxyanisoles with several reagents (*293*); methylated sugars with aniline phthalate (*31*); isonicotinic acid hydrazide with picryl chloride (*102*); octamethylpyrophosphoramide, via dimethylamine, by Dowden's method (*188*); the groups ≡C—CH— and ≡C—S—S—C≡ by an involved procedure (*443*); desoxycholic acid with vanillin (*367*); digitoxin with 3,5-dinitrobenzoic acid and benzyltrimethylammonium hydroxide (*366*); heptachlor with ethanolamine in potassium hydroxide (*364*); hexoses with chromotropic acid in 15*M* sulfuric acid (*252*); ethylenediaminetetraacetic acid, via nickel, with dithiooxalate (*111*); and 2-(*p*-*tert*-butylphenoxy)isopropyl-2-chloroethyl sulfite, via ethylene oxide, with lepidine (*184*).

Many organic substances are determined through some reaction involving an inorganic substance. Thus, one can determine nitrosophenylhydroxylamine diazomethane through colchiceine (*164*, *374*), and gentisic acid (*469*) with iron(III); diacyl amides with ammonium hydroxide, sodium hydroxide, and a buffer (*365*); vitamin B_{12} with cyanide (*385*); methionine with disodium nitrosopentacyanoferrate (*387*); 3-indolebutyric acid with mercuric sulfate in sulfuric acid (*26*); isonicotinic acid with trisodium pentacyanoaminoferrate in glycerol and acetic acid (*203*); amides, via hydroxamic acids, with ferric chloride (*43*); benzene hexachloride with aniline and vanadium pentoxide (*360*); rutin with aluminum chloride (*457*); amino acids and peptides with copper (*427*); and many organic compounds by first treating with an excess of a suitable oxidant, the unused excess then reacting with the dye Fast Green FCF (*175*). Heteropoly complexes serve here, ascorbic acid (*75*) and isonicotinic acid hydrazide (*350*) reacting with molybdophosphoric acid, and acid hematin (*173*) with tungstophosphoric acid.

PHYSICS

In considering the measuring operation, items of concern are the laws of absorption, principles of measurement, and instruments.

Laws of Absorption. As Bouguer's law is one of the rare generalizations to which there is no known exception, it is not surprising that nothing new has been reported on it. Beer's law, however, is still the object of attention. Strong (*440*) derived the Bouguer-Beer law by use of the probability of photon capture, with extension of the monochromatic case to that of a finite band width. The validity of Beer's law was reviewed by Luck (*278*); deviations therefrom are classified by Berger and Verbestel (*42*) as real errors, due to chemical modifications in the absorbing complex, and as apparent errors, due to instrumental factors.

Cannon and Butterworth have warned against assuming that conformity to Beer's law indicates linearity of response of a photocell (*77*). Although the work of Vandenbelt *et al.* (*466*) was in the ultraviolet, it is well to bear in mind their reported failure of Beer's law near the transmittance limit of a solvent.

Strong (*441*) has proposed as a unit for molar absorptivity, the Beer. Whereas molar absorptivity, a_M = liters per centimeter per mole, 1 Beer = 1 square meter per mole.

Principles of Measurement. Nomenclature and symbols remain unsettled. A joint committee report of the American Society for Testing Materials and the Society for Applied Spectroscopy (*214*) suggests a nomenclature for applied spectroscopy. A joint commission of the International Council of Scientific Unions (*25*) recommends that the unit of wave number, hitherto designated as cm.$^{-1}$, be named the kayser with the abbreviation K, and that the symbol σ be used for wave number instead of ν (reserved for frequency).

Photometric errors and their evaluation received further attention. Subjects treated include errors in spectrophotometry (*136*, *339*), methods of calculating relative analytical error (*287*), the appraisal of photometric values for the Spekker photometer (*268*), variability with the Beckman spectrophotometer (*81*), correction for turbidity (*151*), the influence of slit width on determination of absorption bands (*5*), and a parameter-free statistical method of m rankings for evaluation of instrumental variables (*401*). Of special interest is a critical report by Goldring *et al.* (*172*) on the precision and accuracy obtainable with the Beckman DU instrument and on the conditions necessary for optimum performance.

The principles of relative absorbance photometry have been extended (*209*), and temperature effects have been considered for this technique (*32*). Related in principle is a variable reference technique (*229*), which consists of comparing an unknown solution with a reference solution, the composition of which is readily variable.

A variation of a reference method involves the determination of one component in a two-component mixture (*3*). A displacement technique (*189*) employs a flat plate of glass in unselected test tubes, readings being taken with and without the insert.

Instruments. Although there is nothing strikingly new, over-all developments have been significant. There are a few new instruments. Most of the developments concern parts, such as light sources, monochromators, absorption cells, detectors, and various accessory devices.

In the following classification, instruments used for chemical analysis are designated as absorptiometers and include comparimeters and photometers. Those used to determine color as color are designated as colorimeters, a practice long followed by physicists.

Comparimeters. Solutions of potassium dichromate and cobalt(II) nitrate are recommended as permanent standards for the standard series determination of molybdenum in steels (*331*). By using an ocular-attached filter, Ikeda (*217*) modified a Duboscq instrument for use instead of a Pulfrich photometer.

Filter Photometers. Various substances, in solution and film form, are recommended as filters for isolating narrow spectral bands from 350 to 930 mμ (*478*). Two pamphlets describe later interference-type filters (*34*, *150*). New polaroid variable-color filters enable one to vary saturation and/or hue of the color passed (*363*). A modified absorption cell facilitates routine work (*50*).

New filter photometers include the Chromatron (*201*); the Biochem absorptiometer (*206*); one using a multiplier phototube

(*195*); one with a "thinking scale" (precalibrated) (*158*); and one with a measuring slit and high transmittance filters (*314*).

Several miscellaneous instruments are not designated as filter photometers, but undoubtedly a filter could be used. Included are a wedge instrument with selenium photocells (*153*), one with a split photocell (*430*), an automatic instrument for indicating absorption fluctuations in a process stream (*125*), one for determining ozone in air through photoelectric recording of the blue resulting from action of liberated iodine on starch (*109*), and a capillary device for quantitative paper chromatography (*174*).

Preliminary work is now under way to establish ASTM performance specifications for filter photometers (*140*). A photoelectric ear densitometer continuously records arterial concentration of T-1824 in the dye-dilution method (*320*).

SPECTROPHOTOMETERS. Selling (*404*) and Stearns (*431*) have summarized new developments in spectrophotometry, with particular reference to dyeing and textile applications. Stearns also reviewed modern trends of absorption spectrophotometry (*432*).

An alkaline solution of potassium chromate has been carefully re-examined as a transmittancy standard (*197*). Adjustment and calibration of spectrophotometers in general (*340*), and adjustment of the Hilger-Müller instrument in particular (*47*), have been discussed.

Hansen (*192*) considered the optimum conditions of illumination for thick samples of very small amounts of substances. Lallemond *et al.* (*266*) discussed the value of the multiplying phototube as a detector. Treiber and Koren (*453*) proposed means for facilitating measurement of very small absorbances.

The merits of a double-pass monochromator have been discussed (*470*), and the Perkin-Elmer instrument of this design has become available (*355*). The Bausch & Lomb grating monochromator, usable with interchangeable sources and a choice of gratings, has an approximate range of 200 to 1400 mμ (*33*). Tyler's feedback photometer (*458*) involves a simple optical system.

Accessories suggested include a water-jacketed cell holder for Hilger instruments (*137*), an ordinate printing attachment for recording the Veeder counter values of the General Electric instrument (*317*), and a color-forming chemical reaction recorder (*257*).

Modifications, especially for the Beckman DU spectrophotometer provide for reflectance measurements (*191*), for a modified wiring arrangement (*84*), for a multipler phototube photometer (*99*) and a multiplier phototube attachment (*36*), for a variable-length cell compartment (*83*), for a cell attachment for ultramicro work (*104*), for 5-cm. cells of limited volumes (*465*), and for micrometer Baly-type cells of variable thickness (*208*).

Two studies concerned modification of the Beckman DU spectrophotometer for automatic operation at 210 to 2700 mμ (*240*) and an automatic relative transmittance attachment for this instrument (*239*). Commercial development of these ideas resulted in the automatic operator for the Model DU instrument (*35*) and the Model DK spectrophotometer (*37*). Process and Instruments (*371*) have another attachment for converting the Beckman DU instrument to a recording spectrophotometer.

British instruments designed to compete with the Beckman Models DU and B are, respectively, the Unicam Models SP500 (*460*) and SP600 (*461*). An attachment for Model SP500 (*76*) provides for measuring paper chromatograms.

Other new spectrophotometers include an automatic photoelectric Soviet instrument (*446*), a recording instrument with double monochromator (*143*), a grating instrument for the ultraviolet and visible (*448*), an instrument which displays on a cathode-ray tube the differences between the absorption spectra of the unknown mixture and the known reference mixture (*110*), and a new model, just announced, of the General Electric recording instrument (*167*).

Investigations dealing with microspectrophotometry include a review of possibilities of errors from lenticular glare (*348*), microscopic arrangements for measuring a single blood cell (*224*), and an instrument for measuring heterogeneous microscopic objects, such as cellulose and wood fibers (*270*).

Of particular interest for measuring reaction kinetics and the spectra of unstable compounds in the visible region are the studies of Chance (*87*) on accelerated and stopped-flow methods. Operational methods and equipment are described. A new rapid-scanning instrument (*6*) shows the transmittance (reflectance)–wave-length curve of a sample almost instantaneously on a cathode-ray tube. A photographic attachment provides for recording one or more spectra for a changing system. The ozone analyzer of Kiffer and Dowell (*246*) is automatic.

COLORIMETERS. From a fundamental viewpoint, spectrophotometers are the best color-measuring instruments. Less complicated devices have long been used, however, and developments continue in the search for still simpler equipment. Stearns (*433*) prepared an interesting chart which illustrates instrumental and other colorimetric relationships, and incidentally shows diagrammatically the complexity of the subject.

Of interest is the new periodical, *Die Farbe* (*378*), first appearing in July 1952. Thus far, it deals broadly with problems of color and its measurement. An "International Bibliography of Color and Adjacent Topics" for the decade 1940–1949 is in press.

Among the new books, "The Science of Color" is the long-awaited report of the Colorimetry Committee of the Optical Society of America. The work of L. A. Jones and a distinguished group representing various color interests, this publication should take place as one of the great committee reports in science (*230*). Although D. B. Judd was a member of this 20-member committee, he has himself published a notable book written from a somewhat different viewpoint (*233*). Much simpler and more specific is Chamberlin's booklet, "The CIE International Colour System Explained" (*86*). Murray's book (*330*) is a new edition.

The initials ICI (for International Commission on Illumination) have been officially changed to CIE (for Commission Internationale d'Eclairage, the original French publication) to avoid possible confusion with Imperial Chemical Industries.

Davis *et al.* (*115*) have extended earlier measurements on the spectral energy distribution of light sources *A*, *B*, and *C*. Two color-matching scales have been developed. Toeldte's study (*450*) concerns the properties of a color scale consisting of iodine solutions, and that of Lynd and Turk (*283*) deals with the preparation of plastic standards for soils and plant tissues.

Kolrausch (*255*) described the color mixture apparatus of Helmholtz-König, together with its calibration and use. Winch reported details (*477*) of a photoelectric apparatus with 5- and 12-foot integrating spheres used at the General Electric Co., Ltd. The subjective color comparator of King and Rodbell (*247*) provides for evaluating a sample in terms of CIE tristimulus values.

The new high-sensitivity, tristimulus filter instrument described by Glasser and Troy (*169*) has been commercialized as the Colormaster differential colorimeter (*297*). Late models of the Hunter instruments have been announced (*163*). The two-filter photoelectric colorimeter of Smith and Huggins (*424*) is designed for classifying ripe tomatoes on the basis of the ratio of readings for a red and a blue filter. Two color predictors for pigments have been patented (*352*, *434*). The reflectometer of Schulman and Klick is a recording instrument (*402*).

APPLICATIONS

The report of a new or improved method of analysis for some constituent always has some scientific interest. From a practical viewpoint, however, the all-important question is whether the procedure will work in a given situation. Thus, a new method for nitrate alone may be worthless in water analysis because of interference by chloride ions. In the words of the late G. E. F. Lundell, practical analysts are concerned with "the analysis of things as they are."

Table I. Photometric Methods for Specific Constituents

Constituent[a]	Method[b]	Reference
	Alloys	
Al(Cu)	Eriochrome Cyanine R	(*361*)
Al(Pb, Sb, Sn)	Aluminon	(*279*)
Al(Mg, Mn, Zn)	Aluminon	(*281*)
Al(Mg)	Solochrome Cyanine RS	(*22*)
As(Pb)	Mo-blue	(*362*)
Be(Cu)	Aluminon	(*282*)
Bi(Pb, Sn)	Thiourea	(*39*)
Co(Al)	Nitroso-R salt	(*442*)
Cu(Al)	NH_4OH	(*415*)
Fe(Cu)	Thiocyanate	(*130*)
Mg(Al)	Solochrome Cyanine RS	(*23*)
Si(Cu, Fe, Ni)	Mo-blue	(*280*)
Th(Mg)	1-(*o*-Arsenophenylazo)-2-naphthol-3,6-disulfonic acid	(*308*)
V (heat-resistant)	Tungstovanadophosphoric acid	(*449*)
Zr(Mg)	Alizarin-S	(*309, 474*)
	Iron and Steels	
Al	Eriochrome Cyanine R	(*218*)
Cr	Dichromate	(*15*)
	Diphenylcarbazide	(*273, 414*)
Co	Tetraphenylarsonium cobaltithiocyanate	(*1*)
Cu	Diethyldithiocarbamate	(*187*)
	Reinecke salt	(*390*)
	Dithio-oxamide	(*274*)
	NH_4OH	(*253*)
Mn	Periodate	(*100*)
Mo	Pyrocatechuic aldehyde	(*409*)
	Thiocyanate	(*234, 235, 267*)
P	Mo blue	(*207*)
Si	Molybdosilicic acid	(*56*)
	Mo blue	(*179*)
Ti	Chromotropic acid	(*383*)
	H_2O_2	(*375*)
U	H_2O_2	(*375*)
W	Thiocyanate	(*179*)
	Metals	
Al(Ca)	8-Quinolinol	(*428*)
Al(Th)	8-Quinolinol	(*298*)
As(Sn)	Mo blue	(*103*)
As(Cu)	Na_2SO_3	(*57*)
B(Al)	1,1-Dianthrimide	(*60*)
Cd(Pb)	Dithizone	(*418*)
Fe(Ca)	1,10-Phenanthroline	(*428*)
Mo(Ti)	Toluenedithiol	(*413*)
Sb(Sn)	KI, NaH_2PO_2	(*103*)
Si(Al)	Molybdosilicic acid	(*13*)
Si(Al, Be, Ca, Zr)	Mo blue	(*78*)
W(Ti)	Toluenedithiol	(*413*)
	Agricultural Materials	
B (soils)	Waxoline Purple AS	(*205*)
B (wood)	Quinalizarin	(*381*)
Cl (insecticides)	Fast Green dye	(*176*)
Cu (sugar products)	Dithiozone	(*258*)
(soils)	2,2′-Biquinoline	(*92*)
(malt beverages)	Zn-dibenzyldithiocarbamate	(*437*)
Mn (soil extract)	Formaldoxime	(*232*)
P (rocks)	Mo blue	(*215*)
P (fertilizers)	Molybdovanadophosphoric acid	(*61*)
	Mo blue	(*467*)
P (plants)	Mo blue	(*295*)
P (limestone)	Molybdovanadophosphoric acid	(*373*)
Na (soil)	Quinalizarin, via UO_2^{++}	(*354*)
	Biological Media	
Ca (serum)	2,3,4-Trihydroxybenzoic acid	(*455*)
Ca (spinal fluid)	Murexide	(*372*)
Cr (blood)	*sym*-Diphenylcarbazide	(*74*)
DDT (human fat)	Schechter-Haller reagents	(*306*)
F^- (urine)	Zr-alizarin	(*69*)
Gentisic acid (serum)	1,10-Phenanthroline, via Fe^{+++}	(*277*)
I (protein)	$Ce(SO_4)_2-H_3AsO_3$	(*327*)
P	Mo blue	(*194, 397*)
Pyrazinamid (blood)	Mohr's salt	(*4*)
Si (blood)	Mo blue	(*11*)
V	8-Quinolinol	(*445*)
	Ores	
Au (minerals)	Gallic acid	(*202*)
Co, Cr, Cu, Ni(ores)	Various methods	(*17*)
Cu (ores)	2,2′-Biquinoline	(*183*)
Th (sands)	2(2-Hydroxy-3,6-disulfo-1-naphthylazo)benzenearsonic acid	(*28, 29*)
	Gases	
Br (air)	Fluorescein	(*44*)
CO_2 (gases)	Phenol red	(*307*)
CN (stack gas)	Na picrate	(*149*)
Ni (air)	Dimethylglyoxime	(*73*)
O (gases)	Pyrogallic acid	(*476*)
SO_2 (air)	Fuchsin	(*462*)
	NH_4VO_3 on gel	(*353*)
H_2O, C_6H_6, EtOH	Indicators on carriers	(*182*)
	Water and Wastes	
NH_3	Pyridine-pyrazolone	(*261, 263*)
BO_3^{---}	Curcumin	(*199*)
Cl	Cyanide, pyridine, amine	(*16, 341*)
ClO_2	$Na_2P_4O_7$, *o*-tolidine	(*161*)
CNO^-	Via NH_3, Nessler's reagent	(*128*)
	Pyridine-pyrazolone	(*264*)
CN^-	Pyridine-benzidine	(*342, 343*)
	Pyridine-pyrazolone	(*407*)
	Chloramine-T, pyridine-pyrazolone	(*260, 262*)
F^-	Al-hematoxylin	(*369*)
	Zr alizarinsulfonate	(*9*)
NO_3^-	Diphenylamine	(*221*)
	2,4-Benzenedisulfonic acid	(*2, 417*)
NO_2^-	Sulfanilamide, *N*-(1-naphthyl) ethylenediamine	(*40*)
PO_4^{---}	Several methods	(*399*)
SiO_2^{--}	Molybdosilicic acid	(*346*)
	Mo blue	(*10, 14, 105, 322*)
SCN^-	Cu^{++}, pyridine	(*260, 264*)
Ca^{++}	Chloroanilic acid	(*256*)
	Picrolonic acid	(*292*)
Cu^{++}	Dithizone	(*119*)
	Diethyldithiocarbamate	(*94*)
Fe^{++}	2,2′,2″-Tripyridine	(*328*)
	4,7-Diphenyl-1,10-phenanthroline	(*422*)
VO_3^-	Tungstovanadophosphoric acid	(*220*)
	Miscellaneous Materials	
Cu (dyes)	Dibenzyldithiocarbamate	(*303*)
Fe (textiles)	8-Quinolinol	(*190*)
PO_4^{---} (chemicals)	Mo blue	(*236*)
Porphyrins (petroleum)	In $CHCl_3$	(*181*)
SiO_3^{--} (alkalies)	Mo blue	(*243*)
S (alkalies)	*p*-Aminodimethylaniline	(*68*)
V (fuel-oil ash)	Molybdovanadophosphoric acid	(*210*)
Cr, Ni, P, V (rocks)	Several methods	(*41*)

[a] Parentheses indicate the major component or the material containing the constituent.

[b] Constituent is determined with the reagent or determined as the compound shown.

Chemical Analysis. Several books, either new or revised, may be mentioned (*89, 246, 269, 310, 311, 482*), particularly the one by Charlot and Gauguin. A Japanese symposium on part of the subject covers a variety of practical applications (*332*). Two extensive bibliographies have appeared, one on photometric measurements for inorganic ions (*435*), and one on uses of Beckman spectrophotometers (*344*).

Composite methods are recommended for a number of constituents in various materials. Examples are nickel plating baths, light alloys and steels (*222*), aluminum-base alloys (*38, 223*), plant material (*131*), silicate material (*213*), silicate rocks (*408*), and water (*126, 198*).

Inorganic Constituents. So many different inorganic constituents are covered in such a variety of materials that a tabular presentation has been adopted to summarize the developments. Only the constituent, the nature of the method, and the reference number are included in Table I.

Such a tabulation may justify some kind of central agency, preferably international, which would pass judgment on what is really worth while among all the methods published.

Organic Constituents. The studies selected here are arranged in groups, three of which represent rather specific kinds of applications.

Biochemistry. *p*-Aminobenzoic acid (*345*), arylamines (*357*), and glucosamine (*400*) in biological material; acetic acid in blood and tissues (*95*); hemoglobin (*438*) and sulfanilamide (*452*) in blood; *p*-aminosalicylic acid (*393*) and streptomycin (*305*) in urine; amino acids by paper chromatograms (*291*); and pentachlorophenates (*196*).

Agricultural Chemistry. β-Carotene isomers in alfalfa (*436*); pectic substances (*288*); nitroparaffins from fumigants on grain (*231*); 1,1,1-trichloro-2,2-bis(*p*-methoxyphenyl)ethane in milk (*96*); piperonyl butoxide in dusts and paper coatings (*228*); dithiocarbamates in dusts, sprays, and spray residues (*97*); and 2,4-D in milk (*300*).

Dye and Textile Chemistry. Indigo on textiles (*276*);

dye-bath concentrations (*114*, *370*); related is prediction of the color of the dye mixture (*112*).

MISCELLANEOUS. Methanol in ethanol (*186*); *m*-aminophenol in *p*-aminosalicylic acid (*12*, *471*); methylcellulose in cellulosic and polyhydroxy substances (*392*); benzoyl benzoate in *N*-butyl acetanilide in clothing impregnant M-1960 (*45*); sodium carboxymethylcellulose in detergents (*49*); dimethylamine in technical methylamines (*429*); and phenolic substances in water (*142*).

Color Specification. The age-old problem of describing or specifying colors is as important as ever. Description in terms of words will no doubt always be attempted. There is a new British glossary of color terms (*62*). Matching in terms of some material color standard seems indispensable in daily life. Slowly technologists and scientists are becoming more objective by using instrumental and numerical specifications.

Nomenclature and definitions have been reconsidered by the American Standards Association (*8*). A number of references deal with problems of color difference specification. Included are a symposium of seven studies (*7*); use of the Color-Eye instrument for plant inspection (*384*); comparison of the MacAdam and the Adams-Nickerson indexes (*219*); dependence of color-mixture functions on choice of primaries (*284*); size of acceptable color differences (*113*); automatic calculation of color differences (*347*); a formula to facilitate computation of fading from Munsell notations (*171*); tables to aid in computing small differences (*67*); and nomographs for converting between Hunter color-difference readings and CIE color coordinates (*48*).

Derby (*120*) considered the feasibility of color matching with the aid of the R-cam on a spectrophotometer, and Reich *et al.* (*376*) employed reflectance measurements to evaluate cotton detergency. Tyler (*459*) compared the merits of tristimulus instruments with a recording spectrophotometer for color control problems.

Zerban *et al.* (*483*) reported the spectrophotometric measurement of the color of over 100 raw cane sugars. Broeg and Walton (*63*) compared various color standards for measurement of sugar cane sirup and edible sugar cane molasses.

The determination of color of industrial wastes was studied by Rudolfs and Hanlon by means of spectrophotometers and filter photometers (*386*). Valin (*464*) considered methods for determining color in water supplies. Koetschau (*254*) found the color of transparent oils to be a linear function of wave number. MacAdam (*285*) made suggestions for calculating numerical specifications from 380 to 770 mμ when the curve available covers only 400 to 700 mμ.

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Infrared Spectroscopy

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THE change from annual reviews to a review every two years has more than doubled the labor necessary to obtain a useful survey of what has happened in a field as diverse as infrared spectroscopy. It has been necessary to discard several hundred references because of space and time limitations. Many of these, no doubt, are of great interest to some segment of the practitioners of infrared spectroscopy. To those who may find this review less comprehensive than those earlier in this series (*229*), the author can only say that he hopes it will be found to be of use in bringing some order to a chaos (*399*).

In addition to the valuable Ohio State University Symposia on Molecular Structure and Spectroscopy held every June, an International Reunion was held in Paris in June 1953. The Optical Society of America dedicated the November 1953 issue of its journal to W. W. Coblentz, where early researches led the way to modern infrared spectroscopy. The Joint Commission for Spectroscopy meeting in Rome (*17*) discussed many items of general interest, and recommended that the unit of wave number hitherto designated as cm.$^{-1}$ be named kayser. Some journals have already started using the symbol K for this unit. A general standardized spectroscopic nomenclature has been suggested (*278*). The National Bureau of Standards–National Research Council collection of spectra and bibliography is well under way, while the ASTM literature-spectra survey has already issued several thousand IBM punch cards on spectra from the literature. The British have standardized their presentation of spectra during 1953 and have started a National Depository. These projects will eventually be great aids to spectroscopists throughout the world.

The usual number of reviews on infrared spectroscopy were published (*46, 269, 343, 363, 370, 392, 393, 548, 582*) with Crawford writing a semipopular discussion (*118*). Projected student experiments were also discussed (*644*).

Several books or sections of books were published on the subject. Foil Miller's section in Gilman's Treatise on Organic Chemistry (*224*) is an excellent survey. Sutherland's review on amino acids in "Advances in Protein Chemistry" (*581*) is useful. Brügel has reviewed the subject in Germany (*80*), while the Landolt-Börnstein Tabellen (*333*) now have a valuable collection of spectra. Bellamy has written an excellent book on "The Infrared Spectra of Complex Molecules" (*29*).

INSTRUMENTATION AND TECHNIQUES

This general subject has been reviewed in two articles by Lippert (*354, 355*). The precision of spectrometers in routine use has been measured (*96*), while methods of removing air absorption (*214, 323*) and the attendent effects (*73*) have been reported. Resolving power and noise in spectrometers have been reviewed (*74*), false energy corrected (*93*), and prismatic curvature of spectral lines discussed (*218*). Two slit-drive systems (*90, 599*) have been devised and a "ghost" band formed with Nernst filaments has been laid (*341*). A reader for single-beam spectra (*94*) has been devised, and the recording of optical density versus linear frequency discussed (*127*). Littrow-type spectrometers have been improved (*512, 624*) while the double-beam type has been worked on (*107, 126, 241, 444, 506*). The Walsh multiple monochromator system has been described and refined (*107, 228, 248–250, 448, 550, 621, 622, 625, 626*).

Infrared sources have been improved with the introduction of the carbon and zirconium arcs (*243, 286, 526*). Nernst filaments have been improved by a new mounting (*241*) and a helium discharge tube used as a monochromatic near-infrared source (*377*).

Filters were discussed (*415, 477*) along with the properties of thermistor detectors (*649*).

The greatest recent improvement in the handling of samples has been the pressed potassium bromide disk technique of Stimson (*570*) and Schiedt (*534, 535*). In some laboratories this technique has supplanted all other solid phase methods. This method also yields alkali-halide windows (*527*). Some difficulties with solid state preparations which are not uniformly distributed are discussed (*294, 344*), while simple methods for handling low-melting solids (*406*) and recovering valuable samples (*406*) have been proposed. Mulling agents and solvents have been discussed (*13*) along with a method for making dispersions with ammonium stearate (*148*). Evaporated film techniques have been studied (*605*) and a lamination method of sample preparation proposed (*531*).

Several far-infrared spectrometers reaching out to 150 microns wave length have recently been constructed (*323, 374, 446, 473, 623, 653*). At the same time there has been an increase in interest in the near infrared (*77, 501, 502*) sparked by the new, fast, sensitive near-infrared detectors (*76, 419, 509, 510, 554*). The results obtained in these two regions are assuming enough importance to merit a later separate section in this review.

The physical and optical properties of window and prism materials, including refractive indices and transmission, have been reported (*3, 18, 19, 20, 332, 475, 482, 499, 513, 536, 565, 652*).

A number of papers have appeared on the problem of calibrating spectrometers in all spectral regions (*4, 150, 391, 398, 481, 497, 521, 602*).

Cell design has been the subject of a number of papers (*153, 160, 317, 362, 427, 504, 568*). Two variable thickness cells have been described (*101, 576*), and rotating cells for double-beam spectrometers have been constructed (*8, 230*).

Infrared gas analyzers devices becoming more popular every year, have been discussed in detail (*42, 147, 267, 319, 394, 420, 627*).

NEAR AND FAR-INFRARED

Spectra in the near region, usually done with high resolution, include those on the following molecules: substituted acetylenes (*288, 529*), barium oxide (*128*), carbon dioxide (*270*), carbon monoxide (*479*), hydrogen cyanide (*149*), hydrogen sulfide (*10*), methane and substituted methanes (*60, 498, 500, 642, 643*), nitrous oxide (*232*), noble gases (*279*), phenols (*655*), uranium halides (*514, 515*), and water vapor (*274*).

Far-infrared spectra from 50 to 700 kaysers include those taken on ammonia and deuterated ammonia (*252, 573*), arsine and phosphine (*572, 574*), dichloroethane (*57*), hydrogen bromide and chloride (*252, 373*), methyl chloroform (*469*), hydrogen sulfide (*373*), several organic molecules (*447*), and water (*373*).

MICROSPECTROSCOPY

Considerable interest has been shown in microscopy in the infrared. Anderson (*12*) has devised a silver chloride lens system while most other workers are using totally reflecting objectives and condensers (*56, 102, 108, 201*).

REFLECTION AND EMISSION SPECTRA

The measurement of reflectivity in the infrared region is increasing in popularity, with two papers describing methods (*7, 146*). Spectra are reported on ammonium halides (*61*), arsenates and phosphates (*445*), herbaceous plants (*219*), magnesium oxide (*530*), and titanium dioxide (*578*).

A general paper on black body emission discusses Planck's equation and the Wien displacement law (*177*), while Penner (*456*) discusses the Doppler effect. Emission spectra are reported on carbon dioxide and monoxide (*476, 601*), the hydroxyl group (*39*), hydrogen chloride (*429*), alkyl radicals, and the nitro group (*579*). More papers may be found listed under Reactions and Combustion.

REACTIONS AND COMBUSTION

The emission from a hydrogen-fluorine flame has been measured (*35*) along with the flame emission from hydrogen bromide (*81*). Reactions other than flames have been studied (*158, 222*) including autoxidation of methyl linolenate (*314*), and the NO$_2$-ethanol reaction (*443*). The absorption of the flame of a simple double-base powder was reported (*641*).

POLARIZATION STUDIES, CRYSTALS, AND INORGANICS

A number of polarization studies are listed in the Biological section, since many natural materials have been subjected to this type of analysis, but specific studies have been made on amides (*326*), diketopiperazine (*543*), substituted nitrobenzenes (*198*), naphthalene (*463, 465*), methyl ammonium chloride (*618*), organic crystals (*389*), KAu(CN)$_2$ (*291*), sodium formate (*430*), sodium nitrite (*428*), rhombic sulfur (*24*), and terylene films (*403*).

Miller's collection of spectra of inorganic materials (*402*) should be available to all spectroscopists. Hornig (*271*) described an isotope dilution method for use with crystals. Other crystals and inorganics studied include: borates (*157*), brucite (*390*), cadmium fluoride (*240*), carbonates (*368, 369*), chlorites (*159*), glasses (*195*), gold smokes (*255, 256*), hydrazine (*139, 223*), hexafluorides (*221, 337*), iodine solutions (*226, 246, 247*), magnesium oxide (*416*), hydrogen nitrate (*105*), hydrogen nitrite (*292*), nitrosyl chloride (*161*), nitrogen pentoxide (*588*), nitrogen trichloride (and chloramines) (*418*), nitrogen dioxide (*417*), nitrogen tetrasulfide (*359*), condensed oxygen (*558*), perchloric acid and ions (*104, 293*), potassium bifluoride (*113*), KBF$_4$ (*339*), potassium hydrogen bisphenyl acetate (*133*), phosphates (*483*), persulfate ion (*455*), quartz (*115, 196, 552*), rocks (*281*), silicon and germanium (*361*), silicate minerals (*338*), sulfur hexafluoride (*338*), and SO$_2$F$_2$ (*461*).

QUALITATIVE ANALYSIS

The general qualitative analysis papers include one on the use of punched cards in the automatic identification of mixtures (*16*), an excellent collection of spectra of aromatic compounds (*92*), and four valuable papers on hydrocarbons (*381, 488, 541, 542*).

Qualitative studies on various types of compounds and on individual compounds include substituted acetamide (*130, 194, 330, 414*), acetyl acetonates (*156*), acetylene and substituted acetylene (*480, 541*), acids including substituted and long-chain types (*33, 197, 204, 211, 239, 299, 555, 556*), acridines (*546*), alcohols (*44, 244, 259, 264, 472, 575, 654*), allenic compounds (*650*), aluminum soaps (*254*), amino acids (*207, 220*), aryl deuterium (*596*), ascorbic acid (*632*), asparagine (*131*), substituted benzene (*342, 407*), barbiturates (*505, 606*), butadienes (*583*), carbinols (*44*), chromatographed samples on filter paper (*30, 276*), citronellol (*635*), coals and coal products (*91, 208, 227*), cosmetics (*99*), organic cyanides and isocyanides (*316, 594*), cyclohexane derivatives (*215, 336*), cyclo-octyne (*52*), cytidine phosphates (*257*), cytosine (*570*), decalols (*129*), detergents (*528*), dextrans (*88*), dicyclohexyl (*215*), diketones (*22*), enantiomorphs (*168*), esters (*197, 207, 347, 555, 556*), nitrate esters (*325*), substituted ethane (*553*) and substituted ethylene (*387*), fats (*345, 346*), flavones (*265*), fluorine metallic compounds (*67*), geraniol (*422*), gladiolic acid (*233*), hydrocarbons (*58, 199, 258*), halomethanes (*474*), indans (*176*), ionones and related compounds (*423–426*), isopropoxides (*28*), ketoesters (*347*), ketones (*503*), lecithins (*15*), lumistanol (*106*), lurenol (*617*), mercapturic acids (*212, 636*), naphtha (*14, 608*), N—N stretching frequencies (*589*), nitriles (*316, 594*), nitro compounds (*260, 496*), compounds of high nitrogen content (*350*), olefins from Bradford crude (*491*), oxonium ion (*51, 192*), oxides-cyclic (*27*), oximes (*452*), ozonides (*70–72, 124, 125, 580*), hydroxypalmitic acid (*591*), reviews on paraffins (*381, 542*), peroxides (*464*), phenanthrene (*280*), phenols (*284, 522*), phenylhydrazones (*520*), organophosphorus compounds (31, 32), phthalides (155), phthienoic acid (205), polymorphism (162, 311), polysaccharides (449), porphyrins (121, 178), propellants (490), propylene (366), pyrimidines (78, 547), quinazolines (122), quinones (21, 303), rosocyanin (34), salicylides (545), sebacates (563), organosilicon compounds (306, 371), soaps (254), sugars (449, 640), organosulfur compounds (194, 245, 489, 597), thioamides (194), terpenes (471), tetronic acids (154), toxaphene (312), tropolone (328), veratrum alkaloids (454), vinyl group (135), water and heavy water (466, 587), and ximenynyl compounds (9).

QUANTITATIVE ANALYSIS

Several general papers appeared in this classification, including a theoretical treatment of the Bouguer-Beer law (571) and a discussion of techniques (511). A differential method for increasing accuracy with double-beam instruments was given (250). Specific analyses reported are alcohol in ether (110), aldrin and dieldrin (217), total aromatics (59), biphenyl in fiberboard (320), purity of carbon tetrachloride (231), chlorinated hydrocarbons (607), hydrocarbons in air (382), halogenated hydrocarbons (49, 69), hexachlorocyclohexane (405), industrial wastes (68), hindered phenols in oils (487), free phenol in resins (562), pyridine bases from coal tar (145), rotenone (123), and water in air (307).

HYDROGEN BONDING

General papers include one on the thermodynamic and spectroscopic properties (532), symmetrical hydrogen bridges (525), crystals (365), and the association band (130). More specific papers have also been published (43, 83, 132, 169, 209, 210, 213, 302, 324, 353, 540, 577, 584, 603, 616, 639).

BIOLOGICAL

The last two years have seen a great interest in the use of infrared in the study of biological problems and natural materials. Steroid studies have been included in this group although they are not all obtained from natural materials. The increased use of infrared is reflected in the total of 18 steroid papers (109, 163, 273, 287, 295–298, 300, 301, 516–519, 523, 585, 604, 619). Other papers related to proteins, synthetic proteins, and the peptide link (1, 55, 170, 171, 200, 202, 203, 206, 282, 313, 348, 409, 412, 413). Bacteria are being identified and studied by spectroscopic means (202, 349, 494, 495, 544, 567). Other papers study aqueous solution of biologic materials (54), stretched hair (173), hypersensitivity disease (6), chlorophyll (633), brain tissue (537), neoplastic tissue (646), ribonuclease (172), phenanthrene metabolism (637), pneumococcal polysaccharides (569), skin (98, 263), wheat germ (112), and wood (321). Last, but not least, the pits of vipers are infrared receptors (82).

POLYMERS

Polymers may be identified by their pyrolysis products (253, 322) without recourse to assignment of all absorption bands. Other degradation studies are comparable (2). Ozone deterioration (11), structure of rubbers (85), polyethylene terephthalate (103), the determination of absorbed water (290), polyethylenes (524), polyisoprenes (507), and linear polymers (611) have also been studied.

ASTROPHYSICAL

This section has been reduced because of the limited interest in the field, but the determination of carbon monoxide in air (41, 360), the collection and absorption of fog particles (308), and the calculation of atmospheric transmission functions (309) should be mentioned.

ABSORPTION INTENSITIES

General papers include two on the use (116) and rules (137) for isotopes, the value of intensities in the interpretation of spectra (335), and the general intensities of vibration-rotation bands (266). The accuracy of intensity measurements is discussed (395), along with the shape of bands in the liquid state (493). Pressure broadening has been studied (40, 53, 470, 612, 613, 634). Specific molecules studied include carbon monoxide (458, 459), carbon dioxide and nitrous oxide (167), carbonyl sulfide and carbon disulfide (380), hydrogen cyanide (283), hydrogen halides (460), methyl halides (26, 533), the carbonyl band (25), ammonia (5), and induced absorption in hydrogen (97).

THEORETICAL AND MOLECULAR

The theoretical part of this section contains the papers of more fundamental and general interest, while the molecular part contains the papers dealing with specific molecules. Overlapping of the two parts of the section is of course, bound to occur.

The more theoretical papers include a modified Silberstein model of anisotropy (396), interactions in vibrating molecules (600), evaluation of zeta sums for interaction in axially symmetrical molecules (364), force constants in polyatomic molecules (136, 592), bond energies and bond distances (225, 277), the character of chemical binding from infrared spectroscopy (397), bond moments from intensities (533), a new relation between potential energy and internuclear distance (356), spectroscopy from the point of view of the communication theory (175, 315), scattering of radiation by spheres (100), selection rules in crystals (620) and in linear molecules (189), sum rules for isotopic molecules (140), thermal vibration amplitudes (138), rotational line widths (457), centrifugal distortion effects (318), calculation of frequencies in molecules with many atoms and little symmetry (166), perturbation theory applied to the F and G matrix method (272), symmetry factoring (117), linear combinations of S-functions (234), the pyramidal XY_3 molecule (436), and absorption induced by static electric fields (120).

The specific molecules studied from a more theoretical aspect include: acetylene and substituted acetylenes (64, 65, 401, 628), allene (143, 366, 408, 451), the amide group (348), arsine (435), benzene and substituted benzenes (180–186, 216, 560), boron fluorides (114), bromoacetyl chloride (421), bromine pentafluoride (86), carbon dioxide (144, 450, 630), carbon monoxide (404), chloroacetone (410), ethylene chlorohydrin (411), chlorine dioxide (152, 433), cyanic and thiocyanic acid (593), cyanuric acid (431), cyclobutanes (330), cyclohexanes (334), cyclopentane (615), decaborane (310), diborine (352), deuterium oxides (37, 38), diacetylene (187, 188, 190, 191, 289), dioxane (385), ethane and substituted ethanes (45, 251, 327, 386, 388, 438, 440–442, 453, 469, 559, 561, 598, 610), ethyl alcohol (23), ethylenes and halogenated ethylenes (79, 119, 437, 440), ethylene oxide (235), ferrocene (357), fluorine cyanide (590), fluoroform (165), formaldehydes (193, 432), furan (236), germanium tetrafluoride (95), germanium tetramethyl (358), hydrogen bromide (595), HD molecule (651), hydrogen cyanide (75, 149, 283, 305), hydrogen iodide (63), hydrogen sulfide (285), hydroxyl deformation (492), methanes and substituted methanes (47, 50, 62, 84, 134, 141, 142, 164, 174, 179, 351, 378, 379, 383, 400, 468, 478, 484–486, 508, 549, 614, 629, 648), methanol (48, 331), methyl cyanide (609), molybdenum and other hexafluorides (87), naphthalene (467), nitric oxide (631), nitrogen trifluoride (645), alkyl nitrites (586), nitrosyl fluoride (384, 566, 647), oxalyl chloride (304, 656), oxygen molecule (268), ozone (275), paraffins (462, 564), phosphine and related compounds (236, 372, 434, 638), pyridine (111), silanes and substituted silanes (89, 261, 551, 557), stibine (262), organic sulfur compounds (237, 375, 376, 538, 539), thiophosgene (151), and water vapor (36).

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Ultraviolet Absorption Spectrophotometry

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THIS review covers the 2-year period since the last one in this series (*177*) was written. The publication of ultraviolet absorption spectra has continued at a rapid rate. Most of these spectra are obtained for the purpose of studying correlations between structure and spectra, and they are not included in this review.

GENERAL TOPICS

A theoretical derivation of Beer's law is given by Strong (*194, 195*) who extends the treatment to include the effect of the finite pass-band of the spectrophotometer. The derivation and validity of Lambert's and Beer's laws are discussed by Luck (*131*) with special attention to a spectrum which consists of overlapping lines. Some examples of apparent deviations from Beer's law reported by Ungnade, Kerr, and Youse (*209*) are attributed by Vandenbelt, Henrich, and Bash (*211*) to low solvent transmittance since they were not observed with 0.02-cm. absorption cells.

Rose (*176*) discusses deviations from Beer's law produced by scattering from suspended particles. A particularly helpful paper by Goldring *et al.* (*81*) treats the causes of departures from theory in spectrophotometry, principally the instrumental factors. Gridgeman (*85*) presents the theoretical background for the evaluation of the reliability of photoelectric photometry and includes a critique of the transmittance-ratio method developed by Ringbom.

Heidt and Bosley (*94*) present methods for calibrating wavelength and absorbance scales of spectrophotometers. The interference maxima and minima produced by a thin layer of air between flat silica windows is used for the wave-length calibration, and a series of square, woven brass wire screens is used for the absorbance scale. The fact that a linear relation between absorbance and concentration of absorber is not adequate evidence of linearity of response of the detecting system is pointed out by Cannon and Butterworth (*38*), who recommend the use of a set of neutral filters.

Brode *et al.* (*32*) report on a comparative survey which includes data on the same materials obtained with 13 Cary and 11 Beckman spectrophotometers. They conclude that the agreement is satisfactory, both among instruments of the same type and between the two types. The reproducibility of measurements made under a variety of conditions with a single Cary spectrophotometer is studied by Forstner and Rogers (*70*), who find that the slide-wire of the log absorbance unit is accurate and that the spectrum obtained with its use is sufficiently reproducible to allow positive identification of unknowns by superposition of spectra.

Hiskey and Firestone (*104*) extend to multicomponent systems the previous work of Hiskey and coworkers on the use of absorbing reference solutions for increased precision. A variant of this method is described by Allen and Hammaker (*4*). They use as reference for the determination of one component in a two-component mixture a solution of the component which is not being determined. Allen and Rieman (*5*) present a short-cut method, related to the base-line technique, for determining one component in a mixture.

A differential method for the spectrophotometric determination of the rate constant of first order reactions is given by King (*117*). McBryde (*135*) points out that for samples of low absorbance no improvement in precision is obtained by enrichment with a known amount of absorber to a concentration at which the analysis error is low. The importance of temperature effects with differential methods when high precision is desired is emphasized by Bastian (*13*) and a method for minimizing these effects is given.

Interesting and informative review papers have been written by Hirt (*101*), Shreve (*184*), and Stearns (*192*). Hirt (*102*) has also prepared a compilation of sources of information on ultraviolet absorption spectrophotometry.

On the subject of terminology, the Joint Committee set up by the American Society for Testing Materials and the Society for Applied Spectroscopy (*106*) has published its Report No. 6, which includes terms related to both emission and absorption spectroscopy. It is evident that these terms are finding increasing acceptance by workers in applied spectroscopy. Strong (*196*) has proposed the "beer" as the name of the unit of molar absorptivity in terms of square meters per mole and the use of the natural logarithm of the transmittance.

APPARATUS

There is continuing interest in modifications of and attachments for the Beckman quartz spectrophotometer. Kaye and Devaney (*114*) have followed their earlier work on a recording attachment with a report on a split-beam, ratio-recording, single-detector recording system with automatic slit width adjustment. A somewhat similar attachment is described by Etzel (*67*), who chops the two beams at different frequencies. Müller (*150*) has written a description of the commercially available system made by Process & Instruments, Brooklyn, N. Y. Beckman Instruments, Inc. (*17*), has recently announced that its recording attachment will be available soon.

A split-beam, ratio-recording spectrophotometer whose optical system is a modified Perkin-Elmer infrared spectrometer has been developed by King (*118*). Arrangements for removing the C batteries from the case of the Beckman spectrophotometer to an external location for convenience are presented by Cecchini and Eicher (*43*) and by Stenius (*193*). For measurement of low absorbances, Treiber and Koren (*207*) have developed a chopper for sinusoidal modulation of the radiation beam.

Hirt and King (*103*) point out that gains in convenience, speed, and, in some cases, accuracy can be obtained by varying absorption cell length rather than concentration in scanning over spectral regions in which the absorbance varies widely. They show how micrometer Baly cells made by Hilger can be mounted in either the Beckman or the Cary spectrophotometer. A variable-length cell compartment is described in detail by Cecchini (*42*), who uses a simple Baly-type cell with an air path for reference.

For a 5-cm. absorption path with limited volumes of sample, Vallee (*210*) employs cells whose inner dimensions are just large enough to transmit the beam of the Beckman spectrophotometer. Craig, Bartel, and Kirk (*48*) have progressed close to the limit in this direction by constructing 5-cm. cells out of 0.7-mm. glass capillary tubing, thus using a sample volume of about 20 cu. mm. Changes in the Beckman cell compartment to obtain the spectra of solid samples are described by Klick, Schumacher, and Stokes (*119*).

An attachment to permit the examination of liquid films with a Beckman spectrophotometer is described by McAdie and Nicholls (*134*). Edwards (*61*) has designed a water-jacketed cell holder for use with the Hilger medium quartz spectrophotometer. For the study of the spectra of solutions at low temperatures, Passerini and Ross (*167*) have combined a metal Dewar flask and double absorption cells for use in the Cary spectrophotometer between 100° and −196° C.

Activity is continuing in the development of instrumentation for the vacuum ultraviolet region. Johnson (*112*) describes a monochromator usable to 95 mμ which is filled with hydrogen at a pressure of 2 mm., the pressure needed to operate the hydrogen arc source. There are no internal windows and sodium salicylate painted on the radiation side of the exit window serves as a fluorescent detector. A grating spectrophotometer is used by Thomas and Schneider (*204*) beyond the limit of quartz prisms.

Bolton and Williams (*23*, *24*) measure intensities in the vacuum region by covering the window of an 11-stage photomultiplier tube with Apiezon grease or zinc silicate to produce fluorescence. Dunkelman and Lock (*58*) find that the RCA 1P28 photomultiplier tube is usable to 175 mμ, and with a quartz envelope it is usable to 155 mμ. As an alternative approach to the detector problem, Hinteregger and Watanabe (*100*) have studied the use of windowless phototubes with cathodes of nickel, tungsten, and platinum. They obtain good sensitivity and reproducibility between 160 and 85 mμ.

Watanabe and Inn (*221*) use a previously described vacuum monochromator with a windowless thermocouple and a photomultiplier tube coated with sodium salicylate to measure intensities of the hydrogen continuum and some of the emission lines of helium. Hammond and Price (*88*) apply an ingenious method of wide applicability to eliminate the effect of stray radiation in their work in far ultraviolet spectrophotometry. They rock a Littrow mirror about its horizontal axis to move the spectral image on and off the exit slit and tune the detector amplifier to the rocking frequency. Potts (*170*) discusses the purification of hydrocarbons for use as solvents in far ultraviolet spectroscopy.

In order to exploit the combination of ultraviolet absorption spectrophotometry and paper strip chromatography most conveniently, a method for moving the paper strip past the exit slit is needed. Paladini and Leloir (*163*) describe a manually operated accessory for the Beckman spectrophotometer, while Parke and Davis (*166*) have developed an automatic scanning device adapted to the Cary spectrophotometer. Deutsch, Zuckerman, and Dunn (*54*) describe in detail an automatic apparatus for supplying a series of eluting liquids to a chromatographic column, passing the eluates continuously through an absorption cell, and measuring the absorbances at four selected wave lengths—in addition to other operations. A triple-beam, nondispersive ultraviolet gas analyzer has been designed and constructed by Warren (*220*).

BIOLOGICAL AND PHARMACEUTICAL APPLICATIONS

Ultraviolet absorption spectrophotometry has become so popular a tool for biological and pharmaceutical problems that it is difficult to keep up with the published applications and methods.

Vitamins. The reproducibility of the Morton-Stubbs correction for irrelevant absorption in the determination of vitamin A is discussed by Bagnall and Stock (*9*, *10*). Prokhovnik (*172*) proposes a simpler correction formula. Reduction of irrelevant absorption in low-potency fish oils is achieved by Dowler and Laughland (*57*) by use of bone meal as a selective adsorbent. Melnick, Luckmann, and Vahlteich (*132*, *144*) report on a collaborative study of the estimation of vitamin A in margarine by several methods including spectrophotometry and present a spectrophotometric procedure for the control of vitamin A fortification of margarine.

Vitamin A in the presence of tocopherols is determined by Ewing, Sharpe, and Bird (*68*) by first carrying out a chromatographic separation on alumina and measuring absorbances at 325 mμ for the vitamin A and at 290 mμ for the tocopherols. Brown (*33*) uses the automatic scanning device of Parke and Davis (*166*) for separation of vitamins A and E by paper strip chromatography followed by absorption measurements. Thymyl *p*-phenylazobenzoate is recommended by Vignau and Debodard (*215*) as a reference substance for the spectrophotometric method of vitamin A determination. This method is also studied by Boldingh (*22*), Anastasi *et al.* (*7*), Martin Perez (*142*), and Swann (*198*).

Cama and Morton (*35*) determine both vitamin A_1 and vitamin A_2 in cod liver oil by combining measurements on the oil at 327 and 351 mμ with those at 620 and 693 mμ on the antimony trichloride complex. Lunn and Morton (*133*) study the spectra of pyridine, pyridoxal, and pyridoxalimine at a series of pH values to develop analytical methods. The device of Parke and Davis (*166*) is applied by Brown and Marsh (*34*) to the determination of riboflavin, pyridoxine hydrochloride, nicotinamide, and thiamine mononitrate. Metzler and Snell (*146*) determine pyridoxal by use of the absorption of the complex with ethanolamine at 365 mμ, and pyridoxal plus pyridoxamine at 323.5 mμ at a pH of 6.7. The determination of vitamin B_{12} is studied by Vargas (*212*).

To estimate ascorbic acid in tissue extracts, Daglish (*52*) applies the shift in the spectrum with pH. He measures the absorbance at 245 and 265 mμ at pH values of 3.0 and 4.6, and finds that the difference at each wave length is a measure of ascorbic acid concentration and that the value of the ratio of the differences is an indication of the presence or absence of interfering absorption. Mariani (*140*) observes the changes in vitamin D_2 with time by spectrophotometry. Frampton, Skinner, and Bailey (*73*) use absorption spectra to follow the separation of oxidation products of *dl*-α-tocopherol.

Fats and Oils. The standardization of spectrophotometric methods for the determination of polyunsaturated fatty acids is studied by Brice *et al.* (*29*), who find that improved results are obtained if the standards are methyl esters of acids purified by physical methods, such as crystallization and selective adsorption. A method for the determination of linoleic and conjugated dienoic acids in the presence of eleostearic acids is developed by O'Connor *et al.* (*159*). Absorption measurements are used by Herb and Riemenschneider (*96*) to study the variables in the conjugation of natural polyunsaturated acids by alkali. In a comparison of methods for determining polyunsaturated fatty acids in cottonseed oils, O'Connor *et al.* (*161*) report that the spectrophotometric method yields consistently higher values than chemical methods. They discuss the factors affecting the accuracy of the spectrophotometric method.

O'Connor *et al.* (*160*) have studied the relation between the condition of cottonseed and the spectral properties of the corresponding oil. A micromethod suitable for the study of the lipide composition of fluids and tissues of living animals and plants is presented by Herb and Riemenschneider (*95*). Wiley, Cagle, and Wilken (*225*) apply measurements of ultraviolet absorption of alkali-isomerized lespedeza oil to obtain the content of monoene, diene, and triene structures. A similar method is applied by Batishcheva *et al.* (*16*) and by Kaufmann *et al.* (*113*). The absorbance at 231 mμ is used by Mead (*143*) to follow concentration changes of linoleic acid during irradiation-induced autoxidation.

Harrison and Wheeler (*89*) use the difference in absorbance at 234 mμ of the peroxide-induced dimer of methyl linoleate and the thermal dimer to study the course of dimerization. Methyl linoleate and its isomers are studied by Jackson *et al.* (*108*). Lembke, Kaufmann, and Farfoletti-Casali (*127*) obtain the diene, triene, and tetraene content of the extracted fats from butter and margarine, and develop a method for estimating the margarine in butter-margarine mixtures. The differentiation of virgin and refined oils is studied by Wolff and Wolff (*226*) with special reference to olive oils. Morris, MacPhee, and Randall (*148*) describe spectrophotometric methods for detecting substitutes in fatty food products such as butterfat, olive oil, and animal fats.

Alkaloids, Drugs, and Steroids. Caffeine and trigonelline in coffee are determined by Kogan, DiCarlo, and Maynard (*120*). They extract the coffee, separate the desired components by paper chromatography, elute with dilute hydrochloric acid, and measure the absorbance at 272 mμ for caffeine and 265 mμ for trigonelline. Cocaine is determined from its absorbance at 233 mμ by Ampuero and Echea (*6*). Seagers, Neuss, and Mader

(*182*) identify and determine *N*-allylmorphine hydrochloride. Biggs (*21*) determines procaine hydrochloride from its absorption at 290 mμ. The absorption spectrum of veratrine is applied to its analysis by Shanes (*183*), who shows that it consists of equal weights of veratridine and cevadine.

Two-component mixtures of strychnine and brucine are analyzed by Bhattacharya and Ganguly (*20*), using absorbances at 252 and 262 mμ. Moorthy, Chatterjee, and Dakshinamurti (*147*) determine nicotine in tobacco by measuring the absorbance of the extract at 259 mμ. To determine nicotinaldehyde thiosemicarbazone in blood, Motchane and Benson (*149*) extract with hexanol and measure the absorbance at 321 mμ. Similarly, *p*-acetylaminobenzaldehyde thiosemicarbazone is measured at 331 mμ. Ungar, Damgaard, and Wong (*208*) determine salicylic, salicyluric, and gentisic acids in trichloroacetic acid by measuring absorbances at 303, 298, and 320 mμ, respectively. Consden and Stanier (*46*) determine homogentisic acid (2,5-dihydroxyphenylacetic acid) by use of excess phosphomolybdate reagent and measurement of absorbance at 355 mμ. They state that this method can be used for phosphate determination with hydroquinone or ascorbic acid as reducing agent.

The determination of *p*-aminosalicyclic acid is studied by Jensen and Jerslev (*110*), Nielsen and Praetorius (*155*), and Rodrigues and Rodrigues (*175*). The hydrolysis of acetylsalicylic acid is followed spectrophotometrically by Edwards (*62*). Goldbaum (*79*) makes use of the shift of the spectrum of barbiturates in going from a pH of 10.5 to strong alkaline solution to determine micro quantities of barbiturates and to differentiate many barbiturates. His method involves the calculation of ratios of absorbance differences at a number of spectral positions. A somewhat similar method, involving the absorbance difference at 239 mμ between solutions at pH 10 and pH 2, is reported by Simonin, Metais, and Weil (*187*).

The spectrophotometric assay of complex antihistamine preparations is described by Banes (*11*), who uses a combination of extraction, chromatographic separation, and absorbance measurements. Ebstein and Van Meter (*59*) determine α-methylphenethylamine in alcohol at 259 mμ. Isonicotinic acid hydrazide is determined by Neuss, Seagers, and Mader (*152*) by measuring absorbance at 267 mμ; they also studied related compounds. A method for the estimation of khellin in human blood is developed by Soloni and Marquez (*191*); this consists of extraction with alcohol, chromatographic separation on alumina, elution with alcohol, and measurement at 250 mμ. Johnson *et al.* (*111*) determine penicillin G in penicillin O (potassium, procaine, or 2-chloroprocaine) by carrying out an oxidation with potassium permanganate and measuring the absorbances at 220 and 224 mμ of the resulting benzoic acid in $0.1N$ ammonium hydroxide.

Sulfa drugs in pharmaceutical preparations are determined by Halse and Wold (*87*) by diazotizing, removing excess nitrite, and measuring absorbance at 380 mμ. According to Cross, Eisen, and Kedersha (*50*), cortisone acetate when treated with alkali shows an absorption maximum at 373 mμ for which Beer's law is valid at low concentrations. Other Δ^4 unsaturated 3-ketosteroids show this maximum. The carbonyl groups in saturated ketocholanic acids are estimated by Pratt (*171*) who uses the absorbance maximum at 285 mμ and a base-line method. For di- and triketo acids with isolated carbonyl groups, the absorptivity is proportional to the number of carbonyl groups. Carol (*41*) determines methyltestosterone by measuring absorbance at 241 mμ. 7-Dehydrocholesterol is determined by Sobel, Goldberg, and Slater (*190*) from its absorption at 281.5 mμ.

Nucleic Acid Derivatives, Proteins, and Miscellaneous. Deutsch, Zuckerman, and Dunn (*55*) and Loring *et al.* (*130*) use separation methods and absorbance measurements to determine the nucleotide composition of yeast ribonucleic acid. Smith and Allen (*189*) also use a combination of chromatographic separation and spectrophotometry to show that the hydrolyzate of yeast ribonucleic acid contains a fraction of greater complexity than the mono-nucleotides. The determination of pentose nucleic acid and desoxypentose nucleic acid is studied by Logan, Mannel, and Rossiter (*128*), and work on the pyrimidine nucleosides is reported by Fox and Shugar (*71, 72*). Shugar (*185*) has also applied a spectrophotometric method to an investigation of the composition of ribonuclease with special emphasis on its tyrosine content.

The two-component system of nitroguanidine and nitroaminoguanidine is analyzed by DeVries and Gantz (*56*), who determine total nitroguanidines from the absorbance at 265 mμ and the nitroaminoguanidine from the absorbance of the nitroguanylhydrazone of *p*-nitrobenzaldehyde in alkaline solution at 385 mμ. The change of creatine to creatinine is followed by Gaede and Grüttner (*77*) by measurement of absorbance at 234 mμ. Sizer and Wagley (*188*) use the change in absorbance at 280 mμ to study the action of tyrosinase on thrombin, fibrogenin, and fibrin. Theorell and Chance (*203*) study the kinetics of reactions involving liver alcohol dehydrogenase by using two monochromators set at different spectral positions with the same detector. The radiation reaching the detector is alternated by a vibrating mirror, and the absorbance at one spectral position and the difference between the two are recorded simultaneously by an oscillograph.

The indirect determination of esterases is accomplished by Hofstee (*105*) by means of their hydrolyzing action on acetylsalicylic acid and related compounds. The salicylic acid produced is obtained from absorbance measurements at 300 mμ. A similar method is applied by Brandenberger and Hanson (*28*) to the determination of acid and alkaline phosphatases using *o*-carboxylphenyl phosphate as a substrate. The measurement of enzymically produced oxalacetic acid is carried out by Greenwood and Greenbaum (*84*) at 280 mμ. Cammerata and Cohen (*36*) and Nisonoff, Henry and Barnes (*156*) use spectrophotometric methods to study the kinetics of transamination reactions of amino acids.

The interaction of glutathione with maleimide and *N*-ethylmaleimide at low concentrations is investigated by Friedmann (*76*). Fraser and Higgins (*74*) determine the amino groups in proteins and their degradation products by treating them with diazotized sulfanilic acid and measuring absorbance at 363 mμ. Goldfarb and Saidel (*80*) find that absorption due to peptide bonds has a maximum near 185 mμ and that measurement at 205 mμ is a basis for obtaining peptide bond concentration. Proteins at various pH levels are studied by Vendt, Dvornikova, and Anina (*213*).

The spectrophotometric analysis of carcinogen-protein conjugates is described by Peck, Miller, and Creech (*49, 169*). The absorption maximum of tromexan at 310 mμ is used by Rieders and Gruber (*174*) to determine this substance in plasma and serum. Khalifa and Salah (*115*) determine hemoglobin in blood from its absorption at 372.5 mμ. Uric acid in fruit products is determined by Tilden (*205*) by separation on paper, solution in concentrated sulfuric acid, and absorbance measurement at 285 mμ. The ultraviolet absorption spectra of nonsaponifiables in lanolin are applied by Lombard, Heitz, and Chevallier (*129*) to a study of their composition.

INORGANIC ANALYSIS

The strong absorption in the ultraviolet region of many simple ions and ion complexes has been increasingly applied to quantitative analysis, particularly at low concentrations. Wadelin and Mellon (*217*) determine microgram quantities of arsenic by forming 12-molybdoarsenic acid, extracting it in 1-butanol, and measuring absorbance at 370 mμ. The absorption of ceric ion at 320 mμ is applied by Bricker and Sweetser (*30*) to the determination of arsenic by means of a titration with a spectrophotometrically detected end point. They (*199*) also apply the spectrophotometric detection of the end point of bromate-bromide titrations to the determination of arsenic and antimony as two-component mixtures.

Lear and Mellon (*126*) determine nickel by using β-mercaptoproprionic acid as a complexing reagent and the absorbance of the complex at 330 mμ. According to Chilton (*45*), copper, cobalt, and nickel can be determined simultaneously as diethylthiocarbamates; the wave lengths used are 436 mμ for copper, 367 mμ for cobalt, and 328 mμ for nickel. The determination of molybdenum in the concentration range 1 to 6 p.p.m. is reported by Markle and Boltz (*141*), who form the thiocyanate complex, extract with isobutyl alcohol, and measure the absorbance at 320 mμ.

The absorption of the thiocyanate complex of niobium in diethyl ether at 385 mμ is employed by Lauw-Zecha, Lord, and Hume (*125*) for the determination of niobium. This element is determined by Telep and Boltz (*200*) by means of the peroxy complex whose absorbance is measured at 342 mμ. Charlot and Saulnier (*44*) also determine niobium with the same complex and, in addition, determine titanium from the absorbance of its peroxy complex at 410 mμ. The simultaneous determination of niobium and tantalum is achieved by Palilla, Adler, and Hiskey (*164*). They form the peroxy complexes in concentrated sulfuric acid and measure absorbances at 285 mμ for tantalum and 365 mμ for niobium.

The use of the absorbance of the peroxy complex of cobalt at 260 mμ in the presence of alkali bicarbonate is reported by Telep and Boltz (*201*). They (*202*) determine cerium by means of its peroxy complex at pH 10, measuring absorbance at 304 mμ. Newton and Arcand (*154*) state that Beer's law is obeyed by the cerous sulfate complex at 296 mμ. Reiss, Hazel, and McNabb (*173*) determine iron from the absorbance of the ferric acetate complex at 337.5 mμ. Bastian, Weberling, and Palilla (*14*) use the ferric sulfate complex in perchloric acid at 320 mμ, and Desesa and Rogers (*53*) use the ferric chloride complex in 6*M* hydrochloric acid at 342.5 mμ. The formation of the ferric perchlorate complex is studied by Sutton (*197*) by means of the absorption maximum at 240 mμ.

The spectrophotometric detection of the end point in a titration with ceric ion is used by Bricker and Sweetser (*31*) for the simultaneous determination of iron and uranium. The application of the cadmium–1,10-phenanthroline complex is studied by Wadelin and Mellon (*216*); they state that interferences make the method impractical for general use. Kruse and Brandt (*122*) report that the absorbance of the zinc–1,10-phenanthroline complex at 270 mμ at a pH of 4.5 gives a very sensitive measure of zinc concentration. This complex is also studied by McClure (*136*). Hines and Boltz (*99*) determine titanium by measuring the absorbance at 360 mμ of the complex with ascorbic acid The absorption maxima of the pertechnetate ion at 247 and 289 mμ can be used to determine as little as 10^{-8} gram of technetium according to Boyd *et al.* (*27*). Rulfs and Meinke (*178*) have also studied the pertechnetate spectrum.

A method for the determination of trace quantities of aluminum in thorium is given by Margerum, Sprain, and Banks (*139*). Adam, Booth, and Strickland (*2*) determine microgram quantities of beryllium by forming the complex with acetylacetone and measuring absorbance at 295 mμ. Bismuth, lead, and thallium are determined individually or simultaneously, by Merritt, Hershenson, and Rogers (*145*) by measurements at 327, 271, and 245 mμ, respectively. The determination of low concentrations of elemental sulfur in ethanol by measurement of absorbance near 270 mμ is described by Heatley and Page (*93*). In order to study the concentration of ozone in the atmosphere, Inn and Tanaka (*107*) have made quantitative measurements in the spectral range 200 to 750 mμ at pressures between 0.3 and 650 mm.

Pappenhagen and Mellon (*165*) determine small quantities of nitrites by using 4-aminobenzenesulfonic acid to form a diazo compound whose absorbance is measured at 270 mμ. Konopik, Derkosch, and Berger (*121*) report that chlorites and chlorine dioxide in water can be identified and determined by measurements at the chlorite maximum near 260 mμ and the chlorine dioxide maximum at 357 mμ. Gee and Deitz (*78*) use a differential method for the determination of phosphate which is based on the formation of the complex with vanadic and molybdic acids and the measurement at 390 mμ of the unknown with respect to an accurately known solution of approximately the same concentration. Mercurous perchlorate is determined by Higginson (*97*) by measuring absorbance at 236.5 mμ.

ORGANIC ANALYSIS

The determination of benzene, toluene, and xylene vapors in air, particularly at toxic concentrations, is studied by Bouillot and Berton (*25, 26*). Berton (*19*) determines individual xylenes in the vapor phase by measuring absorbances at 268.6, 270.5, and 272.2 mμ for the ortho, para, and meta isomers, respectively. Norris and Coggeshall (*158*) carry out an approximate determination of the C_9 and C_{10} aromatics by dividing them into four classes—mono-substituted, ortho- and meta-substituted, parasubstituted and 1,2,4-trimethylbenzene—and treating the sample as a four-component mixture. They state that the accuracy is only fair for the individual classes, but the total is more reliable.

To detect and determine low concentrations of polynuclear aromatics in waste water, Wedgewood and Cooper (*222, 223*) extract with cyclohexane, adsorb on an alumina column, elute with cyclohexane, and examine the ultraviolet spectrum. Kusama and Koike (*123*) determine 1-methylnaphthalene and related compounds. The reduction products of cyclo-octatetraene are analyzed spectrophotometrically by Craig, Elofson, and Ressa (*47*). Wanless, Eby, and Rehner (*219*) apply ultraviolet absorption qualitatively to characterize the polynuclear components of petroleum products. Eby *et al.* (*60*) employ ultraviolet spectrophotometry as one of several nonbiological methods for predicting the carcinogenicity of high-boiling petroleum fractions. Some of the components in such fractions, particularly anthracene, pyrene, and perylene, are identified and their concentrations are estimated by Schnurmann, Maddams, and Barlow (*180*).

Bateman and Cunneen (*15*) use absorption at 250 mμ as a quantitative measure of extent of styryl conjugation in a study of the tautomerism of phenylpropenes. Wadley and Anderson (*218*) describe a differential method for determining dienes in gasoline and other hydrocarbon fractions in which part of the sample is treated with a diene-removing agent and is used as a reference for the other part at 235 and 258 mμ. Barusch *et al.* (*12*) identify β-dicarbonyl compounds in cool flame combustion of hydrocarbons from their spectra; *n*-pentane forms 2,4-pentanedione and *n*-butane forms butanal-3-one.

Carney and Sanford (*40*) analyze mixtures of cresol isomers by measuring absorbances at 273 (meta), 277 (ortho), and 286 mμ (para). Mixtures of the ortho and para isomers of α-phenylethyl phenols are analyzed by Hart (*90*), who utilizes the absorption maxima at 273 and 285 mμ, respectively. He points out that this method can be applied to other pairs of ortho-para alkylated phenols. The determination of the individual components of technical pentachlorophenol is described by LaClair (*124*). Campbell and Tacker (*37*) determine low concentrations of *p-tert*-butyl catechol added to butadiene as an oxidation inhibitor by evaporating the sample to dryness, dissolving the residue in water, and measuring the absorbance at 279 mμ.

The determination of resorcinol in hair dyes is carried out by Newburger and Jones (*153*) who extract with hydrochloric acid and measure the absorbance at 273 mμ. For qualitative confirmation the spectrum is then obtained for a solution in dilute ammonium hydroxide. A general method for following the course of dichromate oxidations in acid solution by measurement of absorbance at 349 mμ is applied by Cardone and Compton (*39*) to the determination of the oxidation number of glycols, aldehydes, and acids. Englis and Wollerman (*65*) apply essentially the same method to the determination of glycerol in vinegar.

A three-component analysis of technical grade bis(*p*-chlorophenyl) methylcarbinol is described by Grummitt, Marsh, and Stearns (*86*). The ultraviolet spectrum of the reaction product of 8-quinolinol with thiocyanogen is used by Fernando, Emery, and Phillips (*69*) to identify this product as 5-thiocyano-8-quinolinol. Small quantities of 2,4-dichloro-phenoxyacetic acid and 2,4,5-trichlorophenoxyacetic acid are determined by Gordon and Beroza (*83*) by carrying out a chromatographic separation of the acids and making absorbance measurements at 284 and 289 mμ. Hill (*98*) determines 2-methyl-4-chlorophenoxyacetic acid in the presence of 2-methyl-6-chloro- and 2-methyl-4,6-dichlorophenoxyacetic acids by using a baseline method and the absorption maximum at 279 mμ.

The determination of methoxychlor [2,2-bis(*p*-methoxyphenyl)-1,1,1-trichloroethane] on paperboard is developed by Jennings and Edwards (*109*). They extract the methoxychlor with cyclohexane and employ the absorption maximum at 230 mμ with a correction for irrelevant absorption. Beroza (*18*) applies a differential procedure to the determination of mixtures of benzyl benzoate and *n*-butyl acetanilide; the reference solution is a known mixture of these compounds in nearly the same concentration as in the sample.

Agarwal and Spagnolo (*3*) analyze mixtures of phthalic acid and phthalic anhydride by separation with chloroform, determination of the anhydride in solution from its absorbance at 291 mμ, solution of the insoluble acid in alkali, acidification, and determination at 276 mμ. The phthalyl content of phthalic acid esters of cellulose and polyvinylalcohol is determined by Malm, Genung, and Kuchmy (*137*) by measurement of absorbance at 275 mμ. Free acid, if present, is separated by ether extraction and is also determined at 275 mμ. To determine diacetyl in low concentrations, Englis, Fisch, and Bash (*64*) convert it to dimethylglyoxime, whose absorbance is measured at 226 mμ.

The two-component system of eugenol and isoeugenol is analyzed by Vespe and Boltz (*214*) using measurements at 282 mμ (near the eugenol maximum) and at 254 mμ (near the isoeugenol maximum). The spectrophotometric bromine titration procedure of Sweetser and Bricker (*199*) is applied by them to the determination of olefins, phenols, and amines. Whetsel (*224*) analyzes mixtures of anthraquinone and benzanthrone dissolved in concentrated sulfuric acid by absorbance measurements at 266 mμ, where anthraquinone is the dominant absorber, and 515 mμ, where its absorption is negligible.

The kinetics of decarboxylation of 2,4,6-trihydroxybenzoic acid at low concentrations in perchloric acid is studied by Schubert and Gardner (*181*), who follow the change in acid concentration from its absorbance in the range 250 to 275 mμ. Gordon *et al.* (*82*) analyze mixtures of aldehydes and ketones by carrying out a chromatographic separation, forming the 2,4-dinitrophenylhydrazones, and measuring absorbance at 356 mμ. Daeniker (*51*) uses infrared and ultraviolet spectrophotometry to detect small amounts of picolines; 3- and 4-picolines and 2,6-lutidine in coal tar are determined by Kimura and Katsumoto (*116*). Elderfield and Rubin (*63*) follow reactions involving 6-methoxy-8-aminoquinoline by its absorption at 250 mμ.

Absorption measurements are made on 8-quinolinol and related compounds over a series of pH values by Näsänen, Lumme, and Mukala (*151*) to study ionization constants. Scheibe and Fauss (*179*) have written a review on ultraviolet absorption by high polymers. Some applications of ultraviolet spectrophotometry to the study of polymer degradation products are discussed by Achhammer (*1*). Haslam *et al.* (*91*) use a combination of chemical and spectrophotometric measurements to detect and determine low concentrations of ultraviolet absorbers and other additives in polymethyl methacrylate and methyl methacrylate–ethyl acrylate copolymers.

To determine pyrethrins in pyrethrum, Shukis, Cristi, and Wachs (*186*) extract, remove solvent by a vacuum distillation, dissolve in ethyl alcohol, and measure absorbance at 227 mμ. The assay of allethrolone is accomplished by Freeman (*75*) by measuring absorbance in ethyl alcohol at 231 mμ. Flavones are identified from the absorption of their ions by Mansfield, Swain, and Nordström (*138*). An indication of the phenolic content of thiolignins is obtained by Enkvist and Alfredson (*66*) by use of the shift in the spectrum between neutral and alkaline solutions. Patterson *et al.* (*168*) use absorption at 280 mμ as a measure of the concentration of lignin in sulfite digester liquor. Low concentrations of sulfite waste liquors are determined by Treiber, Kleinert, and Wincor (*206*) from absorption at 278 mμ.

Ultraviolet absorption spectra are applied by Olsson and Brandberg (*162*) to the identification of the rosin acids in wood tar. Hastings (*92*) finds that the absorption at 308 mμ of the complex between aliphatic sulfides and iodine provides an analytical method which is sensitive to 1 p.p.m. of sulfur as sulfide. Andreev and Gindina (*8*) determine low concentrations of carbon disulfide at 318 mμ and acetone at 275 mμ. The kinetics of hydrolysis of thiol esters are followed by Noda, Kuby, and Lardy (*157*) who use absorbance at 231 mμ as a measure of thiol ester concentration.

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X-Ray Absorption and Emission

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THE title of the present review has been expanded to give explicit recognition to the increasing importance as a practical analytical method, of x-ray fluorescence—of x-ray emission spectrography, as most analytical chemists will no doubt prefer to call it. This increasing importance, and the continuing interest in the other methods reviewed here, are evident from Table I, where information is given about three recent symposia devoted exclusively to x-ray methods.

Almost all of the papers of the first symposium appeared in ANALYTICAL CHEMISTRY for May 1953. Only one of the other papers has so far been published (*80*), but those of the third symposium will soon be released as a special technical publication of the American Society for Testing Materials.

Inasmuch as the recent literature shows that European activity in x-ray analytical methods is growing, it is somewhat surprising to find only one reference (*106*) in the "Proceedings of the International Congress on Analytical Chemistry," Oxford, to the methods under review.

Willard, Merritt, and Dean (*125*) devote a chapter to x-ray methods in the second edition of their book on instrumental methods of analysis. A review by Shaw (*113*) also covers many of the methods considered here.

X-RAY ABSORPTION

The field is reviewed here under three headings adopted in earlier reviews (*87–91*). In conformity with the expanded title, x-ray emission (x-ray fluorescence) is discussed separately.

X-Ray Absorption Spectrometry. In this method, which was originated by Glocker and Frohnmayer (*59*), the absorption of x-rays is measured at wave lengths that bracket an absorption

Table I. Symposia on X-Ray Methods

Symposium	Date	References
X-Rays as an Analytical Chemical Tool, 122nd National ACS Meeting, Atlantic City	Sept. 16–17, 1952	(*7, 30, 31*)
X-Ray Fluorescence Spectroscopy, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy	March 4, 1953	(*5, 6, 32, 33*)
Fluorescent X-Ray Spectrographic Analysis, 56th Annual Meeting, American Society for Testing Materials, Atlantic City	June 29, 1953	(*2, 3*)

edge. Qualitative and quantitative results are obtained concomitantly.

A significant step to advance the method may have been made by Drahokoupil (*39*), whose work is available here only in abstract form. He describes a recording instrument in which two x-ray beams differing slightly in wave length bracket an absorption edge, so that differential absorbance across the edge can be measured directly. It will be recalled (*87*) that the Dow x-ray absorption spectrometer has a single beam.

The monochromatic (or nearly monochromatic) x-ray beams required in this method are ordinarily obtained either by filtering or by diffracting polychromatic beams. Engström (*45*) in 1947 reported using suitable characteristic lines excited by polychromatic beams for this purpose; thus, the $K\alpha$ line of nickel (1.66 A.) and that of cobalt (1.79 A). were used to determine iron (K-absorption edge, 1.74 A.). Rogers (*110, 111*) has demonstrated that newly developed beryllium-window x-ray tubes provide beams of such high intensity as to increase the attractiveness of the foregoing scheme for producing monochromatic x-rays. Splettstosser and Seemann (*117, 118*) independently accomplished the same result, as their published microradiographs show.

Engström (*28*) has summarized his important work on the use of long-wave-length x-rays in the assay of biological materials. Though this fascinating activity differs a good deal from analytical chemistry as usually practiced, an examination of references to Engström's recent work (*43, 44, 46, 57–89, 100*) is sure to prove rewarding. The improved historadiographic apparatus described by Clemmons and Aprison (*34*) is a welcome indication that this field of research is receiving increasing attention in the United States.

The crystalline form and valence state of an element can be determined in some cases by considering the fine structure on the low-wave-length side of the absorption edge (*66, 82, 127*). Ordinarily, of course, the effect of chemical state on x-ray spectra can be neglected.

Absorptiometry with Monochromatic Beams. Some of Engstrom's work falls in this category. Hughes and Wilczewski (*68*) use a monochromatic beam of wave length 0.71 A. for the determination of sulfur in hydrocarbons.

Coppens (*35*) discusses the application of this method to analytical problems in mineralogy. Zircon ($ZrO_2.SiO_2$) absorbs the $K\alpha$ line of molybdenum (0.71 A.) much less strongly than xenotime (YPO_4), and this provides an easy and certain means of distinguishing between two minerals of otherwise nearly identical physical and mineralogical properties. By making measurements at one or more additional wave lengths, it is possible to distinguish minerals such as the foregoing from others—e.g., sphene, $CaTiSiO_5$—that contain no heavy elements.

Absorptiometry with Polychromatic Beams. The petroleum industry continues to use the method extensively for the determination of tetraethyllead in gasoline; sulfur in hydrocarbons, and additives to lubricating oils (*85, 86, 91, 96, 106, 108*).

Mottlau and Driesens (*96*) have estimated that the time saved by making sulfur and tetraethyllead determinations on a General Electric x-ray photometer paid for the instrument in less than 8 months.

The following quotation (*27*) summarizes the usefulness of the General Electric x-ray photometer in the atomic energy program.

> Without disclosing security information we can state that at present we are making 10,000 heavy metal ion determinations annually by means of the x-ray photometer and that we expect this number to increase as we find new applications among essential materials, process reagents, and others. We estimate that use of the instrument saves approximately 3000 man-hours annually. This figure is estimated on the basis that analysis of a single solution by x-ray requires 20 minutes, whereas other methods require twice this time.

The determination of uranium (*8, 9, 84, 109*) is probably typical of those referred to above.

Norton (*99*) used point-to-point exploration with a polychromatic x-ray beam as a means of selecting uniform thin-walled bulbs for experiments on the diffusion of helium through various glasses.

The use of polychromatic x-rays for thickness gaging and nondestructive testing (*4, 54, 70, 71, 92*) is expanding rapidly, and only a few new examples can be mentioned. The coming on the market of cadmium sulfide detectors has contributed to this expansion (*50, 51, 63, 67, 72–76*); one interesting application of such a detector, the measurement of wall thickness on an aircraft propeller, is illustrated in Figure 2 of (*91*). Ettinger (*47*) describes a differential thickness gage employing two x-ray beams from a common source, and two scintillation counters as detectors. In checking the filling of artillery shells, the gage can detect and record voids as small as 10^{-4} cubic inch in the path of one beam, if the path of the other is void-free. A third application is described as "a fully automatic x-ray inspection system which checks the internal condition of each orange and routes it into one of six classifications, depending on internal condition, at the rate of 10 a second (*42*)." But even this is not all—the equipment compensates for outsized oranges too!

X-ray absorption by gases is potentially important in two kinds of measurements outside the realm of analytical chemistry—namely, that of density in supersonic flow (*126*), and that of elevated gas temperatures (*123*). The latter application, being of more general interest, deserves more attention than it has so far received.

Finally, Brewster's compilation of absorption coefficients (*21*) of special interest for ceramics, and several articles on coal and minerals (*14, 16, 38, 66*) indicate a growing appreciation of methods based on x-ray absorption in two fields where they should prove useful. A recent book (*61*) dealing with the nondestructive testing of metals places methods involving γ-ray and x-ray absorption in correct perspective relative to the older ways of accomplishing such testing.

X-RAY EMISSION

General. At the present time, no instrumental method of analysis is growing in popularity so fast as is x-ray emission spectrography. As with other x-ray methods, the principal factor responsible for this growth is the improvement in methods for measuring beam intensity, but the availability of stable x-ray sources powerful enough to yield characteristic ("fluorescent") x-rays of increased intensity has also contributed.

The analytical chemist unfamilar with the method will do well to regard it as analogous to ordinary emission spectrography carried out on a direct-reading instrument. The earlier history is given by von Hevesy (*65*). Recent reviews by members of the Naval Research Laboratory (*19, 53*), where the method has been under investigation for more than 5 years, are excellent summaries of recent progress, which makes it possible to concentrate on general observations here.

The fundamental facts of atomic structure ensure that x-ray emission spectrography will appear to greatest advantage in the determination of the metallic elements, either free or combined. In the periodic table, the proportion and industrial importance of these elements increase with the atomic number; as everyone knows, the most important nonmetallic elements are found in the region of low atomic numbers. This region is poorly suited to the practical application of x-ray emission spectrography because it harbors serious problems arising from the long wave lengths of the characteristic x-ray lines.

The general position of x-ray emission spectrography is strengthened further because certain of the metals to which it is readily applicable—e.g., the rare earths, the platinum metals, hafnium and zirconium, niobium and tantalum, tungsten, molybdenum, uranium—have grown greatly in importance, and remained difficult or cumbersome to separate or determine by wet methods.

Mode of Excitation. Provided the energy requirements are satisfied, the characteristic lines can be excited by exposing the sample either to electrons, or to x-rays, or to both. Owing to the great convenience of using sealed x-ray tubes, electron excitation—though first in the field (*65*)—is virtually forgotten today. It is well to remember, however, that the most precise results recorded in x-ray emission spectrography appear to be those obtained on a copper-zinc alloy by Eddy and Laby (*41*) by use of electron excitation. In precise work, deviations caused by absorption become important. These deviations decrease with the depth of penetration of the exciting beam. Electrons penetrate to, say, 10^{-5} cm. in the case of aluminum, and less deeply for heavier elements (*122*). Koh and Caugherty have shown that the measurable penetration by x-rays is more than 200-fold greater in a typical case (*77*). Similar values were obtained by Schaal (*112*).

Deviations Caused by Absorption. In present practice, the intensity of a characteristic x-ray line is usually measured by counting. Knowing that x-ray spectra are relatively simple, one might expect that the atomic percentage of an element in an unknown, U, should be given by the proportionality

$$(\%)_U = [(\text{corrected counts per second})_U/(\text{corrected counts per second})_S](\%)_S \quad (1)$$

where the standard S is the pure element. Unfortunately, this simple situation is not realized [see, for example, Friedman and Birks, Figure 7 (*52*)].

By "deviation caused by absorption" (*26*) is meant the difference between the atomic percentage present of an element in a sample U and the atomic percentage calculated from Equation 1. Such deviations arise from three causes that may operate in the sample: absorption of the incident beam (x-rays or electrons), absorption of the characteristic line being used for purposes of analysis, and strengthening of such a characteristic line owing to absorption of a characteristic line generated in the matrix (all of the sample except the element being determined).

These deviations can be dealt with as follows: by selecting standards virtually identical in composition with the unknowns (*23*); by calculations employing relatively few coefficients measured on elements (*78*) or on known mixtures (*115*); and by calculations from the known properties of the elements (*56, 60, 97*). The first procedure is safest when high precision is needed, but it is the most troublesome; the second is a welcome way of reducing the number of standards necessary; the third can probably cope with the first two causes of the previous paragraph but usually requires an arbitrary assumption in case of the third.

Resolution (*19, 22, 26, 53*). This highly technical subject will be dismissed with the following general observation.

The simplicity of x-ray spectra is not great enough to eliminate all problems involving the resolution of x-ray lines. Some of these problems concern x-ray lines of the same series and almost identical in wave length; others arise because second-order K-lines of lighter elements occasionally overlap first-order L-lines of some that are heavier. Attainment of high resolution usually means loss of intensity, so that a workable compromise must be sought in equipment designed for analytical applications. It is usually advisable to operate any given equipment at the maximum intensity and the lowest resolving power satisfactory for the job in hand.

Instruments. The two x-ray emission spectrographs in common use are diffraction instruments modified as necessary (*12, 13, 93, 94*). A helium path is now available to extend the range of the Philips instrument into the region of low atomic numbers (*13*). Birks (*17*) has described a vacuum spectrograph built at the Naval Research Laboratory with the same end in view. An abstract (*20*) of an article by Blokhin gives evidence of Russian activity in this field.

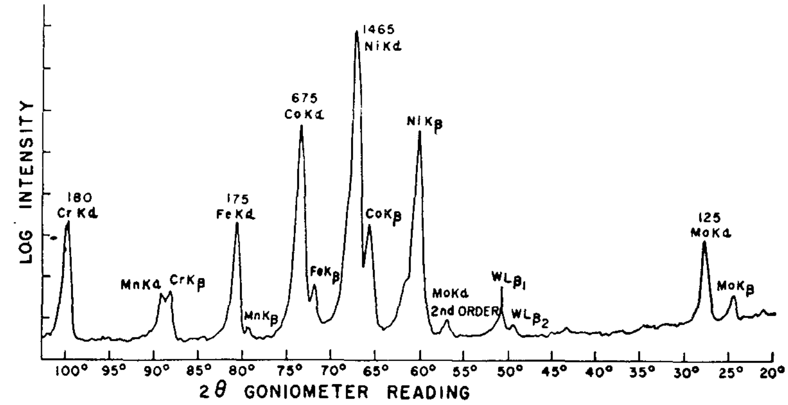

Figure 1. Chart Recording from an X-Ray Emission Spectrograph for a Typical High-Temperature Alloy

Hasler and Kemp (*64*) describe an x-ray analog of the Quantometer in part as follows:

> This all-purpose unit can be fitted with minimum equipment consisting of two channels to allow ratio recording, when first obtained. Subsequently it may be expanded to fill any research or production control need as required by the laboratory. With eight channels, data can be gathered eight times as rapidly as with the conventional single channel instruments and by the utilization of ratios, the instrument may be used under adverse plant power conditions as well as under ideal laboratory conditions.

There is little doubt that the future will bring a variety of instruments designed specifically for x-ray emission spectrography.

Determination of Major Constituents. Perhaps the area of greatest potential usefulness for x-ray emission spectrography today is the routine determination of all the major constituents in the complex alloys being developed for high-temperature applications. When the range of compositions possible is narrow, and when reliable standards in appropriate number are available for purposes of calibration, this application is also one of the simplest.

The analysis of a high-temperature alloy, for its major constituents by x-ray emission spectrography, is now routine at the Thomson Laboratory, General Electric Co. The exploratory work that made this possible was done by Brissey (*22–26*), who used the General Electric XRD-3 spectrometer goniometer in conjunction with the General Electric SPG fluorescence analyzer. A chart recording for a typical alloy appears in Figure 1, in which numbers representing approximate counts per second have been given for the five $K\alpha$ lines used for the quantitative determinations. The chart itself is useful for qualitative or semiquantitative work, but for highest precision the corrected counts per second for each element are obtained from the time required for a preset number of counts at the goniometer setting corresponding to the maximum intensity of the appropriate $K\alpha$ line. Calculation of the corrected counts per second, for use in Equation 1, involves proper subtraction of the background.

On ten samples from the same production lot, Brissey's results yielded standard deviations (*26*) ranging from 1 part in 189 of element present (cobalt) to 1 part in 74 (nickel). The corresponding values for Eddy and Laby (*41*) were 1 part in 274 (copper) or 1 part in 100 (zinc). These data are cited to show the precision attainable under favorable conditions, but a discussion of precision is deferred (see, however, *26*).

Noakes (*98*) has reported results on major constituents for alloys analyzed by both ordinary and x-ray emission spectrography.

Mortimore and Romans (*95*) have reported the successful use of x-ray emission spectrography as a routine control method for the determination of zirconium and hafnium in materials from various stages in the production of these two metals.

The following references are of interest in connection with the determination of major constituents, but they contain other important information also. Patrick (*103*) gives valuable illustrations drawn from the field of ceramics. Carl and Campbell (*29*) discuss the x-ray emission spectrography of minerals. It is clear from their work that the technique deserves serious consideration for the examination of all minerals in which an element of interest is high enough in atomic number to be accessible with the spectrograph available. Despujols' (*37*) work leads to a similar conclusion. Koh and Caugherty (*77*) give the results of experiments designed to test the usefulness of x-ray emission spectrography not only for the simple analysis of alloys, but also for the study of oxide films on them, and of nonmetallic inclusions and of substitutional phases in them. Gillam (*55*) and Gillam and Heal (*56*) have examined the method critically and done searching experiments from which they reach sound conclusions, of which one ("analysis by x-ray fluorescence has a limited application in the rapid works analysis of steels") seems conservative.

Determination of Traces. Great efforts are being made to extend x-ray emission spectrography to the determination of traces, and these efforts are proving surprisingly successful. Counting times are necessarily long, so that great instrumental stability is required. The background count becomes extremely important in establishing the limit of detection, inasmuch as a fluctuation in this count can make it seem that the element sought, though absent, is present.

High in importance among the various trace determinations are those of tetraethyllead, bromine, and sulfur in various hydrocarbon media (*19, 80, 83, 90*) and of metal compounds added to lubricating oils (*36*). Data are also available for iron in blood and for uranium in aqueous solution (*19*). Trace determinations in minerals are covered in references already given (*29, 37*).

Kokotailo and Damon (*80*) introduced an internal standard, selenium, into a trace determination by x-ray emission spectrography, the determination being that of bromine in liquid hydrocarbons. This interesting innovation invites comparison with the well recognized use of internal standards in ordinary emission spectrography. The cardinal point to remember is that, owing to the great simplicity of x-ray spectra, the proximity of selenium and bromine in the periodic table made certain in advance that either element could qualify as a satisfactory internal standard for the determination of the other. Similar assurance does not generally exist in emission spectrography at ordinary wave lengths. The considerations governing this selection of selenium are essentially those that made it possible for Eddy and Laby (*41*) to dispense with calibration curves in their precise analysis of copper-zinc alloys. Finally, the use of selenium as internal standard permitted Kokotailo and Damon to eliminate counting the background at bromine concentrations of practical interest. This amounts to correcting for the background in an arbitrary fashion characteristic of the calibration curves. It does not, of course, remove the effect of fluctuations in the background.

X-Ray and Ordinary Emission Spectrography. It is too early to allocate areas of effectiveness to each of these two emission methods. Noakes (*26, 98*) has carried a valuable comparison of these two ways of analyzing alloys containing the four elements nickel, chromium, manganese, and molybdenum. Stoss and Scott (*120*) have applied ordinary emission spectrography in the analysis of alloys resembling those of Brissey (see *26*, Table II). In both comparisons, comparable precision was attained with the two methods. Of course, precision attainable is not the whole story, much of which lies in the future.

Coating Thickness. A previous review (*89*) included a description of the published work of Beeghly (*10*) on an x-ray method for determining the thickness of tin coating on steel. In this method, absorption by the tin coating of background "fluorescent" x-rays excited in the steel was used to indicate coating thickness.

Recently, Pellissier and Wicker (*105*) have revealed that a similar method has been under investigation by the United States Steel Co. since 1946. Equipment for measuring the thickness of tin coating on a steel base "in the mill on a routine basis has been developed and is in service at all tin-plate producing mills" of that company [for a description of similar equipment, see (*11, 107*)].

INDUSTRIAL FLUOROSCOPY

The field of industrial fluoroscopy has been discussed recently by O'Connor in an excellent article (*101*), in which he stated:

> The development of powerful x-ray tubes and high quality screens has, in the last ten years, resulted in a remarkable number of successful industrial fluoroscopic applications. Those of us concerned with critical inspection problems tend to lose sight of the fact that many types of inspection, though comparatively easy, are still important. Fluoroscopy is doing a big job in these fields and often is the only nondestructive method of inspection which is used.

RADIOACTIVE ENERGY SOURCES

It is not surprising in the present era that x-rays as applied to analytical problems should encounter increasing competition from β- and γ-rays derived from radioactive energy sources. It seems safe to say that each of these rays will prove useful enough in this area to survive, because their properties are different enough to make each superior for certain applications. In particular, it would not be surprising to see β- and γ-rays become more important than x-rays in thickness gaging and similar applications, where the principal objective is the determination of the amount of matter, irrespective of composition in the beam.

If radioactive energy sources continue to grow in importance to analytical chemistry, they will be discussed in a future review. Meanwhile, the following collection of references on γ-rays will, it is hoped, be sufficient present indication of their usefulness:

General information on γ-ray sources, uses, and costs (*40, 48, 69, 79, 92, 114, 124*)
Low energy γ-ray sources (*124*)
Thickness gaging (*4, 40, 81, 102, 114, 121, 124*)
Radiography and nondestructive testing (*4, 15, 40, 48, 62, 69, 79, 92, 102, 114, 124*)
Level gaging (*40, 102, 114, 121*)
γ-Ray exploration (*104, 119*)
Density of concrete (*116*)
Analysis of ancient metallic objects (*1*)
Fluidization studies (*121*)
Density of fluids flowing in closed pipes (*4*)

DETECTORS

Cadmium sulfide crystals are photoconducting and have high dark resistances; hence they can serve as x-ray detectors (*50, 51, 63, 67, 72–76*). When used in this way, however, they do not yet meet the stringent requirements imposed by highly precise analytical work. Their compactness, simplicity, ruggedness, and low cost make it desirable to consider them for all other problems involving x-ray detection.

Scintillation counters are gaining in prominence. These devices were mentioned briefly in the 1949 review (*87*) [in which read Figure 4 for Figure 1 in the sixth complete paragraph on page 23].

The scintillation counter has an interesting history (*18, 49*). Some 50 years old, it was crowded out about 20 years ago by the Geiger counter as a means of counting individual particles or quanta. The replacement of the human eye by the multiplier phototube has revitalized the scintillation counter, however, and the photomultiplier-scintillation counter turns out to be preferable to the Geiger counter for certain applications [for further discussion, see Friedman, Birks, and Brooks (*53*)].

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X-Ray Diffraction

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WHEN the officers of the Division of Analytical Chemistry of the AMERICAN CHEMICAL SOCIETY decided to feature an x-ray symposium at the Atlantic City meeting in September 1952, it was an immediate recognition of an important area in the entire field of instrumental techniques." These are the opening words of G. L. Clark (*25*), symposium chairman, in his introduction to the symposium. This event points up the growth of this technique to an important position in the field of analytical chemistry. In the 2 years since the last review in this journal there have been continued developments in apparatus and technique which have contributed to this growth. These developments and some recent applications are reviewed in this paper.

APPARATUS AND TECHNIQUE

The basic x-ray diffraction equipment available commercially has remained virtually unchanged. Geiger counter–type diffraction units have been increasing in popularity. Jones (*61*) has described a highly stable x-ray unit capable of a high degree of reproducibility. The design and operation of a precision Geiger-Müller counter x-ray diffraction spectrometer have been described (*29*).

There have been a number of modifications and adaptations of existing commercial equipment for particular applications. Smallman (*101*) has described a special sample holder for the Noreleco high-angle spectrometer. An x-ray spectrometer for polymer studies has been discussed by Krimm and Stein (*67*). Irving and Breazeale (*59*) have described an adaptation of the Noreleco spectrometer for fiber studies. A critical evaluation of the Noreleco spectrometer for elastic strain measurements of metals has been given by Maloof and Erard (*78*).

The measurement of x-ray intensities continues to be the subject of a great deal of work. Lang (*71*) has discussed the use of proportional counters in x-ray diffraction work. The use of this type of detector is particularly attractive because of its large usable range. Arndt and Riley (*6*) have compared Geiger and proportional counters for the measurement of x-ray intensity. Williamson (*119*) has discussed the use of the Geiger counter in x-ray studies. Evans (*37*) has described an arrangement for the use of a Geiger counter to measure the intensities from small single crystals. The adaptation of a Geiger counter to a Weissenberg camera has been described (*26*).

A monitor for measuring x-ray beam intensities has been presented by Hargreaves and coworkers (*47*). Eastabrook and Hughes (*33*) have developed a circuit for the elimination of dead time corrections in monitored Geiger counter measurements.

Bertin (*11*) has described an electronic method of image amplification which is applicable to the visual presentation of x-ray diffraction patterns. An integrating photometer for x-ray intensity measurements has been described (*3*). Beu (*14*) has discussed some of the variables involved in the use of x-ray film for the quantitative measure of line intensities. Variables in x-ray film development have been discussed (*28, 111*). Levinson (*74*) has described a method of improving contrast in diffraction films, particularly where fluorescent radiation is involved.

Huxley (*58*) and Yudowitch (*126*) have discussed the optimum conditions of geometric design of x-ray diffraction cameras to yield high resolution and accurate line breadths. Taylor (*108*) has designed a large-diameter adjustable Debye-Scherrer camera. Shielding devices to prevent stray radiation from between the x-ray window and camera have been described (*1, 7*). Young (*124*) has described a jig for the alignment of specimens in the

Philips powder camera. A device for alignment using the x-ray beam has been developed by Beu (*13*).

There has been considerable activity in the field of high and low temperature diffraction. Berry and Henry (*10*) have described a modified mount for a high temperature camera. A high temperature furnace has been described by Walker and coworkers (*116*). Low temperature crystallography has been discussed by Post and Fankuchen (*90*). Low temperature powder cameras have been described by Tombs (*110*) and Wood (*120*). A low temperature Weissenberg camera has been developed (*103*). Calhoun and Abrahams (*23*) have designed a low temperature specimen holder for the Noreleco spectrometer.

A number of cameras and techniques involving microbeams have been described. Gay and Kelly (*41*) have designed an oscillating specimen holder for a microbeam camera. A microbeam camera (*51*) and spectrometer (*109*) have been described. Spark (*102*) has developed a simple method involving tilted plates to obtain microbeams.

Wild (*118*) has discussed the conditions for automatic focusing for a double crystal spectrometer. Aluminum monochromators for high intensity beams for use in powder work have been described (*46*). Birks and Brooks (*15*) have developed a method involving a tennis ball for the uniform plastic bending of single crystals for focusing x-ray radiation. Shenfil and coworkers (*99*) have described a point focus monochromator for small-angle diffraction work.

Small-angle scattering has been the subject of several papers. Yudowitch (*125, 127*) has discussed the general techniques, interpretation, and application of the method. Riseman (*95*) has presented a method of calculating particle size from small-angle data. Banerjee and Martra (*8*) studied small-angle scattering from monochromatic x-rays. Small-angle scatter at long wave lengths has been discussed by Henke and Dumond (*49*). Interference effects in small-angle scatter have been discussed (*86*). Finean (*38*) has described a versatile camera for small-angle studies. Rapid small-angle scattering measurements with a concave mirror and fine focus tube have been described (*34*). Dexter (*31*) has discussed the small-angle scattering from cold worked solids.

Alexander (*4*) has discussed the effect of vertical divergence on x-ray diffraction lines. The effect of lattice imperfections on x-ray line broadening has been discussed by Paterson (*89*). The measurement of x-ray line breadths has been discussed (*5*). Warren and Averbach (*117*) presented a method for the separation of cold work distortion and particle size broadening.

Straumanis has described the techniques (*104, 105*) and applications (*104*) of precision lattice constant determinations. A method for annealing metal powders for precision lattice constant determinations has been presented (*114*). Raeuchle (*92*) has described a method for measuring the diameter of circles in precision determination of lattice constants. Tables for computing lattice constants of cubic crystals have been prepared by Parrish and coworkers (*88*).

Wood and Towsley (*121*) have described a manganese filter for removing FeKB radiation. Shurtz (*100*) has described a method for the direct determination of interplanar spacings from chart recorded x-ray patterns.

A method for direct quantitative analysis by a diffraction absorption technique has been described (*73*). Klug (*65*) has discussed quantitative analysis of powder specimens with a Geiger counter spectrometer.

APPLICATIONS

The application of x-ray techniques to the characterization and identification of a large variety of crystalline compounds has continued. The papers referred to here represent a broad sampling of the various applications that have been made.

X-ray structure determinations of compounds of interest to analytical chemistry have been discussed by Merritt (*80*). An x-ray study of contaminated barium sulfate precipitates has been described (*106*).

Several catalyst systems have been investigated, including Fischer-Tropsch iron catalysts (*77*) and nickel-copper coprecipitation catalysts (*62*). Mosesman (*84*) has carried out an in situ x-ray study of molybdena-alumina catalysts.

The surface structure of colloidal silica and alumina has been investigated (*48*). Ervin (*35*) has carried out an extensive study on the structure of the aluminum oxides. Milligan and Holmes (*81*) studied the system Al_2O_3–SnO_2–TiO_2. Gallium oxide and its hydrate have been studied (*96*) and a phase study of the system PbO–$PbBr_2$ has been carried out (*70*).

Schwartz and coworkers (*97*) have studied the products of chromium trioxide decomposition. Eubank (*36*) has investigated the calcination of magnesia. Hughes and Smith (*56*) have described the rapid quantitative analysis of rutile and anatase in mixtures of the two. X-ray studies have been carried out on cadmium iodide (*123*), the system of rubidium chloride and potassium bromide (*122*), the system of silver and copper mercuric iodides (*107*), and boron carbide (*42*). Engine deposits have been studied by x-ray examination of solid state reactions (*69*).

In the past few years there has been a steadily increasing number of applications to organic chemistry. Sodium soaps (*113*) and soap crystallites (*112*) have been studied. Walker and coworkers (*116*) have studied graphitized carbon. Amines have been identified by the x-ray patterns of their chloroplatinates (*44*). *N*-Alkyl groups (*85*), trinitrofluorenone derivatives of aromatic hydrocarbons (*52*), salts of di- and triaminoguanidine (*87*), tetrazole derivatives (*22*), diglycerides (*55*), and *n*-octadecenoic acids (*76*) have been characterized by x-rays. Rice and Snowden (*93*) have presented the diffraction patterns of dinitrophenyl derivatives of phenyl compounds. The powder patterns of picrates of alkylpyridines have been described by Janz and Solomon (*60*).

Low temperature studies of cyclopentane and neohexane (*91*) and thiophene (*2*) have been described. Crystallographic data on organic compounds have been presented as a monthly feature in this journal.

X-ray work has been done on coal (*82*) and jute (*98*). Kern (*64*) has discussed the use of x-ray analysis on pharmaceuticals. An x-ray study has been reported on aureomycin and terramycin (*32*).

A considerable amount of work has been done in the field of high polymers. Crystallinity and amorphous order in polymers have been studied (*66, 68*). Little (*75*) has used x-ray methods to study radiation effects on polymers. Polychlorotrifluoroethylene (*63*) and polythene (*54*) have also been studied by x-ray methods. The size of latex particles has been obtained by Danielson and coworkers (*30*) and Leonard and coworkers (*72*). The size and arrangement of colloidal particles in relation to x-ray scatter have been discussed (*9, 94*). Meibohm and Smith (*79*) have investigated small-angle scatter from synthetic organic fibers.

In the field of metals and minerals there have been many applications, only a few of which are given here. The structural changes during fatigue (*21*) and creep (*45*) in metals have been studied. Preferred orientation has been studied by Holdin (*53*) and Chernock and coworkers (*24*). Hutchison (*57*) has studied line broadening in copper-iron alloys. Order and atomic arrangement have been studied for copper-platinum (*115*) and gold-nickel (*39*). The system iron-nickel-chromium has been studied at high temperatures (*27*). Beu (*12*) has described a method for measurement of retained austenite in hard steel. Goldschmidt (*43*) has studied carbides in alloy steels. Cold-worked aluminum has been studied by the microbeam technique (*50*).

Bradley has discussed analysis of minerals (*17*). Black (*16*) has described the analysis of bauxite exploration samples. The swelling of montmorillonite has been investigated by Mooney and coworkers (*83*). Brindley (*19*) has discussed line broadening in clay minerals. A high temperature study of the polymorphism of magnesium silicate (*40*) has been carried out. The criteria for the characterization of several clays and minerals have been given by Bramao and coworkers (*18*). The orientation of micaceous minerals has been investigated (*20*).

From the sampling of applications given above, there can be little doubt of the growth and importance of x-ray diffraction in the field of analytical chemistry.

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Electron Microscopy

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ELECTRON microscopes have been generally available for less than 15 years. The small group of a few persons working with the early designs has grown in this brief period to number thousands working with a dozen different makes of instruments in as many countries. Transmission magnetic-type instruments are now commercially available in Britain, France, Holland, Japan, Sweden, Switzerland, the United States, and Russia.

Although about 750 electron microscopes have been installed in different laboratories throughout the world, the ultimate design of the instruments has by no means been established. The flexibility in design goes along with the varied advances that have been made in electron microscopy. The growing use of this research tool has established this new science in its proper role in the study of the microstructure of matter, particularly in the solid state.

Since 1951 (*75*), progress has followed a significant trend. Although applications of electron microscopy have become broader and techniques more specialized in this already highly specialized field, the work reported is more concerned with mechanisms of behavior and functions or processes of growth and degradation. This, of course, presents the more difficult but more important type of laboratory problem. It usually involves the design and execution of properly planned and controlled experiments and often the use of other equipment and methods, in order to corroborate, revise, or fill in existing theory and information. "Snapshot" electron micrographs by enthusiasts do not make for a science of electron microscopy, any more than manipulative skills with an instrument make for an electron microscopist. Because of the many variables associated with related problems, a broad knowledge of the major concepts and principles of the basic disciplines is necessary for the logical interpretation of the data obtained. It has been wisely said that the most important part of any microscope is the brain above it. In keeping with this more discriminative and critical attitude, evaluative and interpretative reviews of electron microscopy in selected fields are appearing with increasing regularity. This is a healthy development because it marks a growing acceptance by those outside the field as well as a maturing perspective by those in the field.

BOOKS

Noteworthy indicators of the increasing level of activity in this field may be found in a survey reported at the Cleveland meeting of the Electron Microscope Society of America in 1952 (*53*). Weber (*171*) listed the instruction in electron microscopy given at 15 foreign and domestic universities. From his own teaching experience and from observations obtained from institutional and industrial laboratories practicing electron microscopy, he made recommendations regarding instruction in instrumental techniques, methods of specimen preparation, laboratory equipment, student supplies, and manuals and books helpful for setting up a graduate course syllabus.

The first book offering a compact and up-to-date text for courses on the theory and uses of the electron microscope has been written by Hall (*71*) of the Massachusetts Institute of Technology. The subject matter includes an outline of elementary electron-optical theory, discussions dealing with the construction and properties of electron lenses and electron microscopes, the interactions of electrons with matter, and the characteristics of electron images. The largest chapter, outlining laboratory procedures in electron microscopy, contains detailed descriptions of techniques for the preparation of specimens. The final chapter includes examples of applications of electron microscopy, primarily in the fields of biology and medicine. Many diagrams and electron micrographs are used to good advantage. An outstanding feature is the set of typical problems at the end of chapters designed to stimulate student interest.

Along this line Fischer has published the comprehensive handbook which he compiled during his teaching of electron microscopy (*63*). The book emphasizes techniques, with examples drawn from both biological and chemical sciences. Related instruments are discussed, including some of the less conventional types of experimental electron microscopes, with particular emphasis upon electron diffraction techniques. These books, in addition to those of Cosslett (*35*) and Wyckoff (*183*), should prove a valuable library for those who wish to obtain further understanding of principles of operation, design, construction, techniques of specimen preparation, and broad areas of application of the electron microscope.

Over the past few years electron diffraction has become increasingly important in the study of crystalline and amorphous materials as well as liquid and gaseous structures. The experimental technique has now reached a high degree of perfection. With this in view, Spink and Feigl have translated Pinsker's book (*126*) from the Russian. Their work brings to the English reader the most recent contributions of the electron diffraction laboratory of the Institute of Crystallography in Moscow. Chapters written by Brockway (*23*) and Heidenreich (*79*) in other books provide reviews of elementary theory and specialized techniques in electron diffraction.

Studies of the physics and chemistry of small crystals by means of a high-resolution electron diffraction camera have been reported in a series of definitive papers by Cowley, Rees, and Spink at the Commonwealth Scientific and Industrial Research Organization, Melbourne, Australia. For example, the size and shape of small crystals (*139*) are evaluated; the occurrence and frequency of stacking faults in gamma-alumina are discussed (*37*); the single-crystal electron diffraction patterns are interpreted from the viewpoint of the morphology of zinc oxide smoke particles (*40*); the effects of secondary elastic scattering of electrons in the form of extra spots, groups of spots, arcs of circles, diffuse bands with sharp edges, and forbidden reflections in single-crystal diffraction patterns are analyzed (*39*); and the conditions governing high resolving power in electron diffraction cameras and those determining the quality of resolution of the fine structure in single-crystal reflections are discussed (*38*).

JOURNALS AND MEETINGS

The first International Congress of Electron Microscopy held in Paris in 1950 was reviewed by Hamm (*75*). Proceedings were published in 1953 (*138*).

Recently a Japanese Society of Electron Microscopy has been formed with a membership of about 600. About 130 magnetic transmission-type electron microscopes of the Siemens-Halske, Shimadzu, Denshi-Kogaku, and Hidachi designs are in use there. In 1953 a Japanese *Journal of Electronmicroscopy* (*89*) was issued as the official organ for publications. Three issues are to be published each year, one in English and two in Japanese.

The German Society for Electron Microscopy is using as its official organ for publication of papers and bibliographies the *Zeitschrift für Wissenschaftliche Mikroskopie und für Mikroskopische Technik* (S. Hirzel, Stuttgart, Germany). Eight issues per year will include practically all areas of microscopical investigation. This group has become rather active in recent years. Wyckoff and Anderson (*188*) official representatives of the Electron Microscope Society of America, reported on the fifth annual meeting held in 1953 in Innsbruck, Austria, where some 300 scientists were in attendance. An interesting breakdown of the 98 papers given showed that only one third were on biological subjects and the remaining two thirds dealt with physics and chemistry. In contrast, at the 1953 meeting of the Electron Microscope Society of America two thirds of the papers dealt with biological subjects. More important, however, was the fact that since the war Europeans have not only caught up with us in techniques but have advanced beyond us with respect to electron-optical developments. Much attention is still being given to the characteristics and properties of electron lenses, and new ways of treating aberrations are being explored from both a theoretical and a practical point of view. It is reported that in a year or two a new Siemens instrument developed by E. Ruska and von Borries will have a resolution of 6 A. The lesson is clear. For some reason, American physicists as a whole have not shown any great interest in electron optics as such. Certainly the number of electron-optical papers appearing at the meetings of the Electron Microscope Society of America have been all too few, albeit the technical quality of the micrographs and papers on applications reached an all-time high at the 1953 Pocono Manor meeting.

The only recent meeting dealing with electron optics was the Symposium on Electron Physics (*115*) held November 5 to 7, 1951, at the National Bureau of Standards in Washington, D. C. This was part of a large number of symposia on special topics in the physical sciences held during 1951 as part of the Bureau's fiftieth anniversary celebration. The Philadelphia annual meeting of the Electron Microscope Society followed the symposium on November 8 to 10. The two meetings together formed a most representative and impressive gathering. The leading workers from Canada, Britain, France, Germany, Japan, and the United States were present. Cosslett (*32*) has reviewed the papers dealing with the fundamental electron-optical and technical problems given at Washington and the contributions concerning specimen techniques and applications given at Philadelphia. He remarked that the most striking feature of these proceedings was that practically all the papers on theoretical optics came from Europe. Hall's (*72*) and Ellis' (*115*) papers on electron scattering, Hillier's (*115*) on interference phenomena in electron-optical images, and the work of Marton, Simpson, and Lachenbruch (*106*) on an electron-optical shadow method of field mapping were noteworthy exceptions.

BIBLIOGRAPHIES

Since publication of the "Bibliography of Electron Microscopy" (listing, by both title and author, nearly 2000 publications from 1926 to 1950) by Marton, Sass, Swerdlow, Van Bronkhorst, and Meryman (*114*), Cosslett's bibliography with abstracts (*31*), and his book (*35*) covering essentially the same period, electron microscopy has been still further developed and applied to new and expanding fields of research and technology. As a result of a survey reported by Moore, Morse, and Dennis at the 1952 Electron Microscope Society meeting, the New York Society of Electron Microscopists (2 East 63rd St., New York 21, N. Y.) has announced a bibliographical service as a means of keeping up to date with the rapidly growing volume of world literature in electron microscopy. Subscribers will be issued listings on Keysort cards (3.3 × 7.5 inches) punched according to both subject and author. The first issue covers the years 1950, 1951, and 1952 (approximately 700 cards). Early publication of references for 1953 and quarterly publications on current literature thereafter are planned. The availability of such a service makes possible further breakdown of the subject matter into the various fields of application according to the needs of an individual worker in a particular field.

As electron microscopy becomes more universally integrated into the methods of research and so absorbed into the general literature, the time will come when the task of compiling a comprehensive up-to-date bibliography of electron microscopy will be as impossible and as pointless as a complete listing of all references dealing with light microscopy. That time, however, has not yet come. For the present and for the next decade bibliographical efforts should be directed toward continuing the compilation and classification of current literature, enlarging the card file to include references prior to 1950, and establishing liaison with the major centers of electron microscopy throughout the world in order to provide a centralized bibliographical service that will be complete, up to date, and classified according to a suitable universally accepted code. Obviously, this is an extremely difficult, but not impossible, task in the present state of electron microscopy, where interests regarding techniques and instrumentation do not follow well-established lines and where the applications do not fall neatly in only one category of the classical divisions of science.

INSTRUMENTS AND ACCESSORIES

The RCA Type EMU instrument introduced in 1944 has been modified and modernized to advantage. The self-biased gun provides increased intensity. The compensable spacer makes possible some adjustment of rotational astigmatism in the objective pole piece. A high-contrast wide angle pole piece giving magnifications from approximately 600 to 6000 diameters is available. A double objective pole piece provides direct magnification in ten steps from approximately 6000 to 80,000 diameters. Very high total magnifications can be obtained without using more than 10× optical enlargement of the electron micrograph, thus avoiding a grainy background from photographic emulsion. The standard pole piece combined with the extended range lens provides, in ten steps, direct instrumental magnifications from approximately 1500 to 20,000 diameters. The intermediate lens modifies the instrument into a three-stage microscope [(after le Poole's (*100*) design incorporated in the Philips and Metropolitan Vickers instruments)] and permits installation of a selected area diffraction stage making possible transmission diffraction patterns of a designated area (as small as a fraction of a square micron) of the specimen as it is seen in the electron microscope. The reviewer hesitates to add the manufacturer's claim that this can be done at the "flick of a switch," because (1) the diffraction stage must be focused precisely on the back focal plane of the objective lens, otherwise readjustment of the objective focus is necessary in order to obtain sharply recorded diffraction patterns; and (2) the usual 1 to 2-mil diameter aperture used to reduce marginal aberrations in the objective pole piece and to increase image contrast must be removed or enlarged to at least 12 to 13 mils in order to see the diffraction patterns and fill the photographic plate. It is not only undesirable and inconvenient but time-consuming to change objective apertures by breaking the column and realigning the microscope. What is needed is an externally centerable objective diaphragm with two or three holes of different sizes. Perhaps the installation of limiting stops in the projector and condenser pole pieces would alleviate the contrast problem. A condenser aperture, as Boadway (*15*) described, would be helpful in obtaining better collimation of the electron beam and reduce electron scattering in the background. In spite of these shortcomings, the modification of the RCA-EMU to a three-stage instrument has many advantages for those working with crystalline materials. Brown and Clark (*26*) have applied this design in crystal-structure analysis of a chromium-nickel-molybdenum steel, using a Metropolitan-Vickers microscope.

These developments demonstrate some of the advantages of the flexible design possible in a vertical column instrument and incidentally some of the advantages of a competitive economy.

Menter has modified the Metropolitan-Vickers EM 3 transmission microscope to permit electron microscopy of opaque surfaces by reflection (*108, 109*). The so-called reflection microscopes are not new, but this modification of a standard instrument gives hope that similar features will be offered for other commercial designs. Although Menter's work will not eliminate entirely the need for replica studies, it provides a decided convenience for quick and direct study of small surface areas of opaque objects by inelastically scattered electrons. A number of others [Cosslett and Jones (*34, 36*), Haine, Hirst, and Ennos (*36*), and Fert and Saporte (*60*)] have reported special designs for reflection electron microscopy. Cosslett, Nutting, and Reed s summary of the Bristol conference on electron microscopy (*36*) outlines (on page 15) the needs of the practical metallurgist in high resolution microscopy and the advantages offered by direct reflection microscopy of surfaces over the indirect replica techniques of transmission electron microscopy.

Refinements made by Reisner (*140, 141*) in the RCA Type EMT permanent magnet electron microscope, such as external alignment of pole pieces, a focusing magnifier for viewing the fluorescent screen through the observation window, and a new 35-mm. roll-film camera for recording more than one exposure per pump-down, are convenient improvements for this low-cost electron microscope.

The new low-cost Metrovick EM4 desk model, with horizontal column using 50 kv. and providing continuously adjustable magnification from 1000 up to 9000 diameters, promises to be suitable for routine work where a resolution above 100 A. is acceptable.

A new vertical column, console model, medium-power electron microscope has been announced by the North American Philips Co. This instrument provides many of the features for which the larger microscope EM-100 (*49*), introduced in 1950, has become known. Magnification is continuously adjustable between 1500 and 15,000 diameters. Accelerating potentials are variable between limits of 10 and 75 kv. Under average operating conditions a resolution of better than 100 A. is claimed for this instrument.

The German AEG-Zeiss represents one of a few electrostatic type models on the market. Rumors indicate that a new electrostatic instrument will soon be available from General Electric in the United States and one from a Japanese manufacturer. Farrand Optical Co. (*55*) has announced a compact electrostatic microscope. Farrand's claims for resolution and image quality are remarkable.

Performance will be the main criterion for evaluating the place of these new instruments in the field. The idea of a truly low-cost electron microscope for routine use in education, industry, and medicine has not been realized. Nothing is available much below $10,000. It appears that such a "student model" will not be forthcoming for some time.

Two papers at the 1952 Electron Microscope Society meeting (*53*) reported heaters for the specimen stage of electron diffraction cameras (*29, 125*). This small furnace fits into the specimen chamber and operates under vacuum. Such an accessory permits studies over a wide range of varied temperatures (ambient to about 1000° C.). Phase transitions may be studied, gas-free surfaces examined, migration and diffusion of solids observed, and rates of reactions in oxidizing, reducing, or inert atmospheres may also be studied with the aid of such specimen heaters. Because heating various materials may evolve more than gas, precautions should be made to shield contamination products from the electron-optical system as well as the vacuum system. Effects of preferred orientation must also be considered in the interpretation of the diffraction data obtained.

TECHNIQUES AND APPLICATIONS

Nonbiological. The physical and chemical applications of electron microscopy are varied and numerous. The methods of dispersion and specimen preparation of particulate materials have been relatively well established and the techniques of replication of surface structures are being applied to an increasingly larger variety of bulk materials. A large part of the contributions of electron microscopy in the fields of the physical and chemical sciences are ancillary to laboratory studies of broad problems or are part of restricted researches sponsored by industrial and governmental organizations, so that the presentation and publication of papers are understandably not as numerous as they might be.

As a result of experiments on the reliability of internal standards for calibrating electron microscopes, Watson, Grube, and Rouge (*168, 169*) have published conclusions important to the practice of electron microscopy. Employing spectroscopy as an independent method for determining the spacing of replicas of diffraction gratings used also as specimens in the electron microscope, they concluded that fresh replicas of ruled gratings are far more reliable and accurate than the unstable particles of polystyrene (Dow Latex 580 G) which became so popular as a reference standard for calibrating instrumental magnifications.

Studies of contrast and grain in electron micrograph negatives by Cravath (*41*) and Hamilton (*74*) indicate that the medium lantern slide emulsion generally used for electron microscopy is not much different from the numerous other types of photographic emulsions and that there is not much point in searching present stocks for superior or special-purpose emulsions for electron microscopy. Current studies and the general problem of photographic recording of electron-optical images are discussed by Cosslett (*33*, page 66). Hope still exists, however, that recent successes with nuclear emulsions will have parallel accomplishments for electron microscopy. Hamm and Comer (*30*) described several preparation techniques which yield specimens useful for obtaining direct visible evidence in the study of latent image theory. A paper evaluating the several types of replica techniques used and the preparation of substrates for high resolution electron microscopy was written as a result of their study on photographic emulsions (*76, 77*).

A definitive paper by Calbick (*27*) discusses the mechanism of formation of inorganic replicas in electron microscopy and the importance of stereoscopic methods in the interpretation of the size and shape of details in the micrographs obtained. The mode of propagation of metallic vapors in shadow casting by vacuum evaporation using gold-198 and chromium-51 is described by Preuss (*137*).

Sennett, McLauchlan, and Scott (*153*), in a continuation of their previous studies of evaporated metals within the specimen chamber of an electron microscope, describe successive observations on the formation of crystallites in cadmium and zinc deposits.

Electron microscopical studies of the surface structures of deformed aluminum, copper, silver, and alpha-brass were interpreted from theoretical considerations of the elementary structures and the mechanism of slip band formation resulting from plastic deformation by Kuhlmann-Wilsdorf and Wilsdorf (*95, 96, 180*). The hardening processes in aluminum were interpreted on the basis of the fine structure of slip bands by Brown (*24*) and further interpretations of the micro-slip in deformed single crystals of aluminum were made by Brown and Honeycombe (*25*) in developing a mechanism of slip. Nesbitt and Heidenreich's (*116*) electron metallographic studies of the physical structure and magnetic anisotropy of Alnico-5 have resulted in the formulation of a mechanism which enables the alloy to respond to heat treatment in a magnetic field.

The chromium-rich precipitate accompanying embrittlement in chromium steels subjected to temperature of 885° F. was identified by means of an "extraction replica" (a type of pseudoreplica) technique by Fisher, Dullis, and Carroll (*65*). This technique (*3, 64*) makes it possible to free from the metal matrix the precipitated particles that are partially embedded in the negative plastic replica, by etching the same replica a second time through the plastic. Selected areas of the replica containing the actual precipitated particles can be examined by both electron microscopy and transmission diffraction. The technique has also been applied to the identification of nitrided silicon steels (*104*).

The excellent work of Subcommittee XI on electron microstructure of steel of ASTM Committee E-4 on metallography was first presented in 1950 (*1*). Extensive studies on electron metallography carried out cooperatively by various companies and members of the committee have continued. Members of Subcommittee XI actively participating in this study are:

W. L. Grube, Chairman, General Motors Corp., Detroit, Mich.
C. M. Schwarz, Secretary, Battelle Memorial Institute, Columbus, Ohio
L. B. Birks, Naval Research Laboratory, Washington, D. C.
R. D. Chapman, Chrysler Corp., Detroit, Mich.
P. Coheur, Centre Belge de Métallurgie Physique, Liége, Belgium
A. L. Ellis, International Harvester Co., Chicago, Ill.
A. Feduska, Hoppenstall Steel Co., Pittsburgh, Pa.
R. M. Fisher, U. S. Steel Corp., Kearny, N. J.
E. F. Fullam, Consultant in Electron and Light Microscopy, P. O. Box 444, Schenectady, N. Y.
A. H. Geisler, General Electric Co., Schenectady, N. Y.
D. J. Girardi, Timken Roller Bearing Co., Canton, Ohio
L. Habraken, Centre Belge de Metallurgie Physique, Liége, Belgium
J. M. Hodge, U. S. Steel Corp., Pittsburgh, Pa.
L. D. Pellier, American Cyanamid Co., Stamford, Conn.
G. E. Pellissier, U. S. Steel Corp., Pittsburgh, Pa.
G. H. Robinson, G. M. Technical Center, Warren, Mich.
F. G. Rowe, American Cyanamid Co., Stamford, Conn.
D. M. Teague (past-chairman), Chrysler Corp., Detroit, Mich.
C. F. Tufts, Sylvania Electric Products, Inc., Bayside, L. I., N. Y.
J. R. Vilella, U. S. Steel Corp., Kearny, N. J.

The second progress report was made on the electron microstructure of bainite in steel (*2*). The third progress report was presented at the 56th annual meeting of the American Society for Testing Materials June 29 to July 3, 1953. Abstracts of eight papers describing and evaluating basic techniques for ferrous electron metallography are given in the program (*3*). These report the results of an extensive cooperative program of study with the electron microscope of the structures of a series of different specimens of eutectoid steel prepared specially for the purpose. The structures studied to date include those resulting from the direct transformation of austenite at various temperatures, such as pearlites and bainites, and those resulting from tempering martensite, also at various temperatures. The purpose of this work was twofold: to gain fundamental knowledge of the structures of steel and, in the process of acquiring this information, to develop techniques of electron metallography that would preclude errors of interpretation resulting from faulty preparation of the specimen or from inadequate replication methods. Ideally, for an absolute evaluation of replica techniques the same area of the same specimen should be used in each separate laboratory. For the purpose, Robley Williams has suggested the use of a marked face of a natural unpolished diamond.

However, as a result of the excellent work performed by the participating members of Subcommittee XI, the investigations thus far provide a sound comparative basis for a general acceptance of techniques and practices as applied to the electron microscopy of steels. Information of this kind should be extremely useful in advancing knowledge of the relationships between the morphology of the structures in steel and the mechanical properties of the material. Reviews of techniques and methods for the examination of metals by electron microscopy and diffraction have made a comprehensive coverage of the progress and possibilities of these modern research methods in physical metallurgy (*79–81, 88*).

Rochow (*143*), continuing his graphic study of natural and synthetic resins which he logically calls resinography, discusses the morphological properties and molecular weights of some silicone polymers. The data obtained from fractured surfaces of polymerized sheets and oily smears of diethylgermanium oxide are interpreted from the standpoint of classical theories of structure and characteristic behavior as a surface active agent.

The effects on the apparent particle size and its frequency distribution arising from the method of specimen preparation, shadow casting, distortion of shape, and other artifacts inherent in the electron microscopy of synthetic elastomer latices (copolymers of butadiene) are evaluated by Stromberg, Swerdlow, and Mandel (*166*).

A report by Dwornik and Ross (*50*) contains a discussion of the preparation of samples and use of the electron microscope in studies of some uranium-bearing minerals. The information obtained from this survey will be useful in supplementing mineralogic descriptions, in guiding and checking separation techniques, and in establishing paragenetic relations of associated minerals in uranium deposits.

Criteria for the characterization of kaolinite, halloysite, and a related mineral found in clays and soils are reported by Bramao, Cady, Hendricks, and Swerdlow (*20*). The specificity of results obtained on the same set of samples by three independent methods—differential thermal analysis, x-ray diffraction, and electron microscopy—are compared and evaluated.

Biological. The direct and continuous observations of living matter in the light microscope have provided the main basis for interpretations of the behavior and function of many of the components found in biological structures. These, however, have been limited by the resolving power of the light microscope. In the electron microscope, present studies of such material made up of complex, three-dimensional, heterogeneous, dynamic systems are physically limited to observations of parts of fixed, dehydrated structures frequently altered by chemical and physical treatment, and the subsequent interpretations of morphological features in the light of related experiments and methods in biology. Fixation, dehydration, embedding, and cutting used in the preparation of thin sections and procedures involving changes in surface tension such as drying in air, vacuum desiccation, and electron beam bombardment are clearly sources of artifact which will require a thorough understanding before the methods used can be properly evaluated. For those actively engaged in research in this field as well as for morphologists generally, the evaluation of results as they appear will be a continuing problem.

Nevertheless, the newer techniques of specimen preparation for electron microscopy, such as thin sectioning (*22, 28, 51, 58, 67, 83, 99, 117, 123, 158, 161*), spraying droplets of suspended material and freeze-drying (*172–179*), and the critical point method (*4–7*) for preserving the three-dimensional structures have opened broader avenues in the study of biological materials. Studies of brochosomes (*167*), protozoa (*62, 87, 94, 131, 146*), bacteria (*14, 18*), cytoplasm (*130*), chromosomes (*17*), mitochondria (*162*), muscle (*13, 124*), nerve (*78, 157*), blood cells (*84, 98*), viruses (*19, 86, 90, 102, 103, 154, 155, 175, 177*), bacteriophage (*97, 119, 176, 177*), macromolecules (*56, 91, 185*), particles associated with cancer (*47*), tissues and their relationships to processes of growth and disease (*92, 101, 110, 111, 155, 178*), and possibly to clinical problems (*142, 156*) have occupied a major part of recent proceedings of the Electron Microscope Society of America (*52–54*).

In 1949 when the method using plastic embedding and thermal advance for cutting very thin sections of biological material was developed at the National Bureau of Standards (*117*), it was stated:

> The ability to produce sections for study in the electron microscope in anything approaching a routine fashion would be of immense advantage to research in almost any field of biology or medicine concerned with the microstructure of such material. Although fixation artifacts remain problems for serious consideration, the new method presented here provides a practical, inexpensive approach to the problem of producing extremely thin sections that have uniform thickness, large area, and integrity of tissue structure.

Even though the mechanisms of fixing, "staining," and dehydrating biological material for electron microscopy have not been systematically explored to the fullest extent and no ideal, single procedure has been found that provides optimum preservation of all features found in biological material, or for that matter, of all the details in a single cell, the studies of Porter at the Rockefeller Institute for Medical Research, New York, Sjostrand at the Karolinska Institute, Stockholm, Wyckoff at the National Institutes of Health, Bethesda, Md., and their associates as well as the work going on in many other laboratories would indicate that, so far, the best fixative is buffered osmium solution or vapor. Formaldehyde in a buffered aqueous solution is also useful for electron microscopy. Because biological fine structures that exist in the living state are not too well known, it is very difficult to establish criteria for good fixation. Poor fixation can be defined more easily. The fixatives which have been so universally accepted for use in light microscopy are not, in general, satisfactory for use in electron microscopy (*133*).

Contrast in light microscopy depends upon the selective absorptivity and transmissivity of chemically stained histological features. Phase-contrast microscopy, like electron microscopy, develops image contrast which depends largely upon differential scattering produced by variations in the thickness and density of the object. In so far as phase-contrast microscopy permits studies in vivo and in vitro of unstained material, comparisons with the electron microscopical features observed in fixed, dehydrated, and sectioned material are fruitful (*47, 181*).

Porter and Kallman (*134*) in discussing the significance of cell particulates as seen by electron microscopy warn that, even though the activity of a viruslike agent can be demonstrated in the case of chicken tumors and the mouse mammary tumor, dense particulates occurring in tumor cells can be the result of poor fixation and other chemical and physical procedures used to prepare the specimens. Palade has made an informative study of (osmium) fixation for electron microscopy (*121*) and a survey of endoplasmic reticulum in cells studied in situ (*122*). These investigators made observations on various types of cells grown in vitro, and although recent improvements in the fixation (*135*) and sectioning of tissues permit equivalent and even broader studies of cell structure, they have used such preparations only to confirm findings made in the cultured cells (*127*). They have sought to define the fundamental fine structure of tissue cell cytoplasm and to determine which submicroscopic structures are common to all cells and to what extent these vary in the normal. Only when these are well understood can morphological observations be extended to pathological tissues (*57, 130*).

At the eleventh annual meeting of the Electron Microscope Society held November 5 to 7, 1953, at Pocono Manor, Pa., Borysko and Sapranauskas presented a dramatic comparative phase-contrast and electron microscopical study of entire colonies of living and fixed, dehydrated, embedded, and sectioned cells grown in tissue culture at the Johns Hopkins Hospital (*54*). Time-lapse phase-contrast motion pictures were made during the entire process to determine whether artifacts were produced. Preliminary electron microscopical studies of cross sections of transplanted cells revealed variations in the extent of vacuolation and granulation occurring in the cytoplasm, and variations in mitochondrial structure, as well as other morphological differences.

A similar comparison using freeze-drying or the critical point method of drying on the same specimens would be very helpful in determining the degree and kind of artifacts arising from the drying process. Parallel experiments involving metal versus glass cutting edges and sliding versus rotary microtomes would prove helpful in appraising the cutting mechanisms. Similarly, complementary studies of polymerized and partially polymerized acrylics and other plastics versus paraffin-collodion embedding materials would serve a useful purpose. Comparative and correlative experiments such as these are necessary in order to remove preconceived notions of structural details determined by persistent procedures in histology developed for light microscopy and to evaluate the morphological details obtained by electron microscopy.

In 1952, Bretschneider (*21*) indicated that application of ultrathin sectioning techniques to electron microscopy has yielded only sparse results. At the National Cancer Institute, Bethesda, Md., Dalton (*42, 44*) in his review of electron microscopy of tissue sections demonstrated the value of the electron microscope in resolving not only cell ultrastructure but also the finer structural detail of these cell components which are grossly visible with the light microscope. With his standardization of fixing, dehydrating, and embedding procedures, the use of enzyme digestions and specific heavy metal impregnation techniques, and the application of the experimental method (*43, 45–48*), Dalton believes that future studies of thin sections with the electron microscope should yield important information, not only in the field of cell ultrastructure but also in the general areas of cytology and cytochemistry.

At the Sloan-Kettering Institute for Cancer Research, Selby (*151, 152*) has also reviewed the electron microscopy of tissue cells. Her 278 references emphasizing cytological studies would similarly indicate the advances made in the short interval since Bretschneider published his review.

At the National Institute of Dental Research, Bethesda, Md., Scott (*148*) reviewed recent contributions in dental histology by use of the electron microscope. Because much time and effort have had to be expended in the development of techniques involving replicas of etched surfaces and ground sections and thin sections of demineralized tissues differentially digested by enzymes, many of the studies have been justifiably exploratory in character. The contributions of some ten laboratories in seven countries have established that much that is new can be learned about the submicroscopic structure of the dental tissues. Further light can be shed on some of the questions that have arisen from earlier studies with light microscopy. The need for a thorough investigation of normal tissues as an antecedent to histopathological studies has been universally recognized. Consequently, most of the information accumulated thus far relates to the structure of normal enamel and dentine (*149, 165*). Preliminary investigations have recently been made on dental caries, periodontal disease, endemic dental fluorosis, and topically applied fluorides as related to the microstructure of dental and oral tissues. From the thousands of micrographs in his laboratory, Scott has selected 40 micrographs to bring out the important point that the major findings of most investigators have been reproducible and to demonstrate the structural variations that are seen even in preparations made without deviations in technical procedure. Data on the specimens from which the micrographs were made are listed at the end of his paper to assist further in the comparative evaluation and interpretation of the findings.

Sjostrand's (*158*, *161*) modifications of recent advances in ultramicrotomes have been incorporated in a design produced commercially by LKB-Products, Stockholm, Sweden. With his sectioning technique he has obtained remarkable sections whose thickness is less than 200 A. (as determined by shadow-casting methods). The thinnest section obtained so far has been so measured to 70 A. This means that the thickness of the sections no longer represents a limiting factor with respect to the resolution that can be obtained, even in dealing with specimens exhibiting pronounced opacity to the electron beam. The limiting factor in the detection of fine structure now lies in the contrast-producing properties of the material being studied. A resolution of 20 to 25 A. has been measured by Sjostrand on ultrathin sections through dense structures, as, for example, the myelin sheath of osmium-fixed myelinated nerve fibers (*157*), and the rod-shaped mitochondria with their double cytoplasmic membranes (*162*), in the retinal rods of the guinea pig eye (*159*, *160*), in the excretory cells of the mouse pancreas and in the proximal convoluted tubules of the mouse kidney (*163*).

The recognition of a number of viruses of plants, insects, and the higher animals within the tissues they infect has been made possible by the development of thin sectioning. The problem of how viruses develop and grow is, however, not so easily solved, because deductions bearing on the course of such a dynamic process must be made from static observations subject to artifacts and because all viruses do not behave in the same way.

Intracellular forms of viruses of the pox group seem particularly well suited to study by the electron microscope because their uniform size, shape, and density and their abundant number and occurrence allow them to be recognized within infected cells cut in thin section. Morgan and Wyckoff's (*111*) study of fowl pox was the first clear demonstration of the practicability of thin sectioning for animal viruses within host cells. Vaccinia-infected chorioallantois has been investigated by Bang (*9*, *10*), who suggested a relationship between mitochondria and virus, and by Wyckoff (*186*), who pointed out certain structures of low density in the electron beam which might have a role in virus development. Using similar material Melnick, Bunting, Banfield, Strauss, and Gaylord (*66*, *107*) at Yale University have called attention to evidence suggesting that cells infected with *Vaccinia*, *Ectromelia*, and *Molluscom contagiosum* viruses all form developmental bodies believed to be virus precursors which are round to oval, slightly larger than mature virus particles, less dense to the electron beam, and of a more varied morphology. Wyckoff, in the hope of seeing how the elementary bodies develop, discusses in a later paper (*187*) an extended examination of many tissue cultures and chorioallantoic membranes diseased for various lengths of time. Though those observations have revealed virus particles even shortly after infection, they have, rather unexpectedly, failed to provide a clear-cut and unequivocal picture of how the particles have come into existence. Evidence indicative of several hypotheses bearing on the growth of the virus particles has not been sufficient to select in any satisfactory fashion among them.

Bacteriophages (*184*) are the viruses which have thus far been most studied with the electron microscope. Their distinctive shape makes them relatively easy to observe within the sectioned host bacteria. Much has been learned about phenomena attending their growth. But as with the insect viruses, there are so many different strains and so many variations in the mode of infectious growth that generalizations are not easily obtained.

Wyckoff (*182*) in a report on the fine structure of protoplasm in healthy and virus-diseased cells discusses methods for studying the relation between the new electron microscopical detail visible in sectioned cells and the fine structure actually prevailing in the living cells. Gelatin prepared in similar fashion shows the same spongelike structure as protoplasm. Its gels can be prepared in more varied ways and they, therefore, are excellent means of studying this relation. Another approach to this problem is through determination of the changes in protoplasmic structure brought about by virus diseases. Such alterations, however, depend on the virus and can consist of protoplasmic depletion, fragmentation, or replacement by other, nonviral substances.

The ability to see detail of macromolecular dimensions in sections cut through cells permits further inquiry into how this detail develops as cells grow and multiply, how the macromolecular solids are built up, and how they are altered by disease. There is no difficulty in sectioning many plant and animal tissues so as to reveal cells in all stages of the mytotic cycle, but the determination of the changes produced in native protoplasm by even the best agents for fixation and dehydration remains for serious and continued study.

As Wyckoff (*185*) points out, many macromolecular solids composed of filamentous particles are products of vital processes. Although studies of connective tissues have not shown the mechanism of formation of muscle and nerve in animals or of cellulosic walls in plants (*59*, *61*, *93*, *105*, *112*, *113*, *120*, *145*), they have shown something about the orderly arrangement of the molecules that make them up. In the case of collagen (*68–70*, *82*, *85*, *118*, *128*, *129*, *132*, *142*, *144*, *147*) these studies in conjunction with x-ray diffraction analysis (*11*, *12*, *16*, *170*), indicate that its fibers must develop through a process that resembles crystallization in being an orderly association of filamentous molecules with a repeat unit which leads to the characteristic periodic (about 600 to 650 A.) striations of the fibers. This repetitive internal structure differs from the usual polyhedral crystal. It is a kind of solid new to crystallography and represents what can arise when molecules of the requisite complexity are brought together under suitable conditions. Similarly, the threadlike macromolecular particles found in actin, fibrin (*73*, *150*), and tobacco mosaic (*179*, *184*) provide additional data leading toward the solution of the problems bearing on the formation and structure of the protein molecule.

In the electron microscopy of biological structures, volatile components and particularly water, which is so essential to its function, must be removed prior to examination. When specimens are dried for study in the electron microscope, the surface tension of the evaporating liquid produces gross distortions of their structures. Anderson (*4–7*), at the University of Pennsylvania, has shown that these distortions can be largely eliminated by raising the temperature of the ambient liquid above its critical point, as it loses the capacity to form two fluid phases, its surface tension vanishes. While in this condition, the ambient fluid is allowed to escape, leaving the specimen behind. Stereoscopic electron micrographs of human red-cell "ghosts," paramecia, bacteria, and viruses prepared in this way demonstrate beautifully that these delicate specimens retain many aspects of their three-dimensional structures. The difficulties inherent in the critical point method have been detailed by Anderson:

> Chemical and physical changes are probably induced by subjecting the specimen to solvents (alcohol, amyl acetate, liquid carbon dioxide) which are foreign to physiological environments. Specimens must always be observed in a chemically fixed state.
>
> Because the technique frequently requires that the specimens be sandwiched between two films of collodion, shadow-casting cannot usually be employed.

The disappointing results obtained from past and current freeze-drying methods have prompted Williams (*172*, *174*) at the University of California, to examine critically the techniques used and to report a method for impinging high velocity microdroplets of suspended material upon a collodion-covered copper surface at a temperature from $-75°$ to $-170°$ C., and for subliming the resulting thin layers of ice at about $-50°$ C. The time taken for such droplets to pass through the freezing point is estimated at about 10 microseconds. The entire time necessary for a freeze-drying cycle from spraying to observation in the electron microscope is about 40 minutes. Satisfactory volatile electrolytes for suspending and freeze-drying biological objects appear to be ammonium succinate and ammonium benzoate. Williams' micrographs so prepared of human red-cell "ghosts" indicate that shadowed fixed specimens are almost perfectly rigid spheres, whereas shadowed unfixed cells exhibit some slumping. From these and tobacco mosaic virus micrographs showing concentrated networks and single particles standing on end, the conclusion is drawn that the new method of freeze-drying preserves three-dimensional structure and that negligible surface-tension forces act upon the specimen during sublimation.

As Williams points out, there are unique advantages potentially associated with the preparation of specimens of this type by freeze-drying:

Either fixed or unfixed material can be used.

The specimen need not be subjected to foreign chemical environments.

The specimen material is instantly frozen into a solid matrix, thus tending to preserve intact the structural relationships existing in the normal aqueous suspension.

Precise qualitative comparisons and quantitative assays can be made of the shape, size, and frequency distribution of particulate suspensions.

Two drawbacks inherent in the method are:

The specimen must be made up of well-dispersed small particles which are resistant to freeze-drying.

Frozen-dried specimens of large size such as bacteria are extremely vulnerable to damage by the electron beam.

CONCLUSION

Because the magnetic transmission-type electron microscope, like the conventional compound light microscope, images objects interposed in the illuminating beam for the primary purpose of delineating the geometrical structure of the specimen, it has become a complementary and supplementary research tool in microscopy. Although the electron microscope, with its hundredfold greater resolution, has inherited many problems beyond the power of the light microscope, many of the accepted techniques used for the study of structures by light microscopy are, however, no longer suitable when these structures are examined by electron microscopy. The extension in vision provided by the electron microscope has made possible new knowledge about solids, inorganic as well as organic. It has reached down to the lower ranges of colloidal systems. In dealing with biological substances, it has made molecular structures visible and has created the hope that further progress will show how these macromolecules are developed through the living processes that originate them.

The major efforts in electron microscopy have, therefore, centered around the problems and methods of specimen preparation and selection. How far the art and science of applied electron microscopy have developed was demonstrated by the consistently high quality and technical excellence of the micrographs and papers presented at the Pocono Manor meeting of the Electron Microscope Society of America. Two symposia held there, one on sectioning and the other on replication techniques, illustrated that the examination of many bulk materials is no longer a major obstacle. Inasmuch as many of the papers were concerned with mechanisms, functions, and processes of behavior, growth, and degradation, the discussions regarding interpretations and concepts were sincerely critical and intensely spirited. Emphasis was placed on evaluation of the microstructures observed rather than on how the specimens were prepared and how the micrographs were obtained. Details appearing in the structures were carefully scrutinized and appraised from the viewpoints of reliability and reality. Indeed, this self-critical attitude for discriminating between facts and artifacts in the interpretation of observations should and must be applied to electron microscopy in general, so that it can continue to grow as a science and in conjunction with other methods further contribute to the present knowledge of the microstructure and properties of materials. The rapid growth in little more than a decade is remarkable and much encouragement can be had from present trends, so that real advancement towards some of the more fundamental goals can be hoped for.

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Chemical Microscopy

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THIS review covers the period from the first review (*184*) to the end of 1952. No effort has been made to cover books or papers appearing during 1953 either directly or through the abstract journals. Some references in metallography and electron microscopy are included where the information given is of particular interest to chemical microscopists.

Several meetings of interest to microscopists have been held during the past five years. The first International Congress of Microchemistry was held in Graz, Austria, during the summer of 1950 (*379*). The Armour Research Foundation held four summer symposia in the field of microscopy: Electron and Light Microscopy in 1948 (*166*), Fine Particles and Resolution in 1949 (*167*), Thin Films in 1950 (*168*), and Surfaces in 1951 (*258*). This series will be resumed in 1954.

Richards (*320–322*) has published a series of studies on the history of the microscope, including a final study on recent advances in microscopy (*323*). Foster has also published a survey on advances in optical design of the microscope (*116*) and books by Langeron (*222*), Wredden (*402*), and Lautenschlager (*227*) cover very well the theory and applications of the microscope. The polarizing microscope is covered in books by Hallimond (*165*), and Hartshorne and Stuart (*169*). A handbook by Freund (*134*) covers industrial applications of the microscope.

The problem of the microscopist in technical work is discussed by Mason (*267*) and the place of the microscope in industry by Greenland (*150*) and Wachtell (*374*). A good general discussion of the applications of the polarizing microscope by Johnson (*185*) has appeared. The correlation of light and electron microscopy was the subject of one meeting (*166*) and at least two studies (*65*, *265*). Barer (*22*, *25*) critically discusses the relative advantages of phase contrast, polarized light, and interference microscopy in achieving resolution and appearance of detail.

GENERAL METHODS AND APPLICATIONS

Vinyl polymers are being used as embedding media for leather previous to sectioning (*290*), as mounting media (*158*), and to seal microscopic cover glass preparations (*33*). Refractive index data for current mounting media (*149*) and for media containing diiodomethane (*89*) have appeared. Dark-field illumination for determination of refractive indices by the immersion method is recommended by Dodge (*95*), and Dollar (*96*) proposes a stage and method for continuous variation of the refractive index during examination of an immersed crystal.

A much needed book on micromanipulation by de Fonbrune, a pioneer in this field, has appeared (*114*). A scheme for electron and light microscopical study of identical areas of a specimen are reported by Hyam and Nutting (*183*). Brandstätter (*59*) discusses the determination of molecular weight using the microscope. Howes (*179*) suggests the use of detergents in the aqueous media when examining difficultly dispersible particles. Pristera (*310*) has developed a means of differential staining of high explosive mixtures such as cyclotol and pentolite so that the non-TNT phase can be studied.

The effect of aging of barium sulfate precipitates and other precipitation factors such as coprecipitation are discussed by Fischer (*112*). Shadowcasting as an aid in light microscopy is suggested by Bhattacharya (*49*). Microscopic measurements of difficultly accessible dimensions (*343*) and of the amplitudes of micro-oscillations (*370*) have been reported.

A very useful technique called dispersion staining has been refined and applied by Crossmon to a number of industrial problems (*82–84*). The sampling and identification of particulate matter in the air have been studied with success by Seely (*350*) and Crozier and Seely (*86*), who impinge the sample on a gelatin-coated slide in which specific qualitative reagents have been dissolved.

Schaeffer (*341*) reports the use of isoquinoline as a reagent for microscopic identification of copper and cobalt in the presence of nickel as well as for the detection of zinc and cadmium. Schuldiner (*348*) identifies amidone (6-dimethylamino-4,4-diphenyl-3-heptanone) by the characteristic precipitates obtained when various inorganic reagents are used. Fischer and Simonsen (*113*) use the electron microscope to study dimethylglyoxime derivatives of nickel, palladium, and bismuth, and Feinstein (*109*) uses 1,2-cyclohexanedione dioxime as a reagent for nickel. The microscopic detection of alkaloids by simple optical tests and characteristic crystal habit is reported by Keenan (*193, 194*). The microscope has been applied to a number of industrial problems such as metal stearates (*73*), coatings (*358, 359*), prepared food mixes (*37, 38*), starches (*69*), catalysts (*144, 384*), foods (*195*), cement clinker (*232*), coal (*294*), insecticides (*373*), minerals (*352*), and nuclear tracks (*32, 81, 99, 219, 376*).

ACCESSORIES

Accessories for the microscope include a new microprojector (*337*), an arm rest (*355*), dichroscopes (*97*), a theodolite stage with advantages over the Fedorov universal stage (*55*), a cell for observing preparations undergoing ultrasonic vibration (*231*), a microcalorimeter (*263*), a simple attachment to increase depth of focus in photomicrography (*303*), modification of an ordinary microscope for petrographic work (*394*), discussion of polarization filters versus calcite (*349*), an aperture transforming unit which raises the N.A. and magnification of an objective by a factor equal to the refractive index of the immersion medium used (*128*), a unit magnification system for long working distance (*102, 148*), and a low-power micromanipulator and microdissector for use at magnifications up to about 200 × (*31*).

The comparison microscope is discussed by McLean (*261*) and a socalled "ultra-acoustic" microscope by Sokolov (*354*). The latter is based on reflection of ultrasonic waves from the object which are then collected on a piezoelectric plate and observed on a cathode ray tube. The instrument is said to permit magnifications of several thousand and is useful for the detection of objects in optically opaque media.

OPTICS

The theoretical aspects of microscope resolution have been treated in detail by Berek (*42–47*), Osterberg (*298, 299*), Stokes (*360*), Martin (*264*), and Françon (*122*) who in a new form of Abbe's experiment on gratings, detects image details below the presumed resolving power of the microscope.

A number of studies on new objectives have appeared (*57, 151–156*). The coating of eyepieces and objectives is discussed by Lane (*221*), Osterberg and Wissler (*301*), Tronnier and Wagener (*372*), and by Wilkins (*386*). Wilson (*393*) discusses tests for objective aberrations and Wooters (*401*) discusses the effect of decentered objective lenses.

The influence of the condenser on resolution is covered by Boltjes and Gorter (*54*), and uniform illumination by Schendell (*344, 345*). The effect of the pupil of the eye on resolving power of the eye has also been studied (*17*). Wolter has carried out a careful study of the images of transparent elliptical cylinders (*397*).

PHOTOMICROGRAPHY

Papers in this field range from photomicrography without microscope or camera (*66*) to an excellent paper by Derby on photomicrography in three dimensions. A useful short text on practical photomicrography has also appeared (*277*). A mechanical stage and focusing accessory for three-dimensional movement of the specimen has been described (*356*). The use of repeating flash tubes has been applied to single-shot photomicrography as well as cinemicrography (*223, 224*).

The use of the Polaroid Land camera has been reported by Hauser (*170*). Color photomicrography is discussed by Weston (*381*) and by Loveland (*235*). The use of auxiliary magnifiers to give unit magnification with long working distance is also reported (*102, 148*). Halliday (*164*), Hauser (*171*), and Ross (*333*) have covered photomicrography of surfaces.

CRYSTALLOGRAPHY

Two excellent books in this field have appeared recently: Hartshorne and Stuart, "Crystals and the Polarizing Microscope" (*169*); and Wahlstrom, "Optical Crystallography" (*375*). Two very complete reviews have also appeared covering crystallographic methods: Mitchell (*279*), on the use of crystallographic constants in identification, formation of derivatives, summary of techniques and methods in optical crystallography, and optical crystallographic data for 24 organic compounds; and Komarek (*208*), who coins the new word "microcrystalloscopy" for the study of crystal properties, crystallization processes, and isomorphism.

Wood and Frank (*400*) have an excellent paper showing one of the ways that microscopic study of refractive indices can supplement x-ray crystal analysis of solid solutions. Griffin (*157*) has studied the unimolecular steps on beryl crystals.

Crystallographic data for 20 derivatives of sulfanilamide have been published by White, Witt, Biles, and Poe (*382*). Larsen, Poe, and Witt have published similar data for the 5-nitrobarbituric acid (dilituric acid) derivatives (*225*) and the 2-nitro-1,3-indandione derivatives (*226*) of amino acids. Hubach and Jones (*180*) have used optical and x-ray properties of derivatives of Methadon hydrochloride as means of identifying this compound.

The Armour Research Foundation continues its monthly publication of crystallographic data. The following compounds have appeared since the last review: 2-methylnaphthalene (*4*), pimelic acid (*5*), benzalaminophenol (*6*), allyl thiourea (*7*), *o*-aminophenol (*8*), zinc acetate dihydrate (*9*), 2-mercaptobenzothiazole (*10*), γ-chlorocyclohexane (*11*), *o*-aminobenzene (*12*), uranyl nitrate hexahydrate (*13*), sulfasuxidine (*14*), dimethylglyoxime (*15*), 2,4,6-trinitrotoluene (*16*), *trans*-stilbene (*239*), uracil (*141*), vanillin (*240*), antabuse (tetraethyl thiuram disulfide) (*146*), β-alanine (*214*), acetoacetanilide (*215*), cyclotrimethylene trinitramine (RDX) (*241*), *sym*-diphenylurea (*242*), *unsym*-diphenylurea (*242*), potassium perchlorate (*242*), cyclotetramethylene tetranitramine (HMX) (*243*), phenylacetic acid (*147*), potassium permanganate (*244*), aureomycin hydrochloride (*216*), nitroguanidine (*245*), xanthotoxin (*209*), tetrazole (*257*), sodium stannate (*210*), sodium metaborate dihydrate (*211*), chrysene (*212*), di-*p*-tolyl selenium dibromide (*289*), 1,8-dinitronaphthalene (*246*), tetrachlorophthalic anhydride (*247*), *cis*-terpinol hydrate (*248*), *cis*-terpinol (*249*), *N*-phenyl-2-naphthylamine (*250*), lanthanum oxalate decahydrate (*142*), ethylene dinitroamine (*251*), 2,4,6,2′,4′,6′-hexanitrodiphenylamine (*252*), β-acetylphenylhydrazine (*388*), phthalic anhydride (*389*), dibenzylsuccinate (*213*), 1,5-diphenyl carbohydrazide (*390*), L_s-threonine (*75*), pseudotropine (*76*), DL-mandelic acid (*332*), 2,4-dinitrophenol (*259*), and 4,6-dinitroresorcinol (*256*).

FUSION METHODS

The general references under this heading include the first edition of the Kofler text, "Mikromethoden zur Kennzeichnung Organischer Stoffe und Stoffgemische" (*204*), a study comparing Kofler's thermal methods and fusion analysis (*254*), an introduction to fusion methods of organic compounds (*238*) and inorganic compounds (*148*), a general study of the Kofler methods (*203*), and an investigation on the microscopic identification of liquids by means of critical solution temperature measurement using sealed tubes with the Kofler hot stage (*111*). A second edition of the Kofler's book (*204*) will appear in late 1953 and an English translation of this edition in 1954.

New hot stage designs include Kofler (*202*), Matthews (*269*), Opfer-Schaum (*295*), Stewart (*357*), and a vacuum furnace for high temperatures by Nichols (*291*). There are also two special heating bars modified and refined by Kofler from the old Dennis melting point bar (*205*), and two studies covering the use of thermistors in cryoscopy are of interest to hot stage designers and users (*408, 409*). Finally, Müller and Zenchelsky (*286*) and Kardos (*190*) have published details of photoelectric sensing and control circuits for the objective determination of phase changes under the microscope.

A number of cold stages have also been reported, among them: Rhodes (*317*), which can be used at −140° C. with an 8-mm. objective; Monier and Hocart (*281*); the Koflers (*206*); Hutchings (*182*); Bouttier (*56*); Mitchell (*279*); and a stage by Cech (*71*) reported to cover the entire range from liquid nitrogen to the melting point of the metal under study.

Mitchell (*279*) in a very complete paper on the use of the microscope for the identification of organic compounds, shows how mixtures of adipic and succinic acids can be identified by their appearance on crystallization from the melt. Kofler (*201*) discusses the use of the hot stage in the study of polymorphism, McCrone (*253, 255*) reports on grain growth and boundary migration using the hot stage, Kofler (*200*) uses the hot stage to study hydrates, Gilpin (*140*) identifies sterols by fusion methods, Arceneaux (*3*) identifies benzene hexachlorides and determines the γ-isomer by melting point depression using the hot stage.

Brandstätter (*60*) uses the micro melting point and refractive index of the melt to identify barbituric acid derivatives. Christenson *et al.* (*74*) use 3-nitro-1,3-indandione as a reagent for about 100 organic bases. Feldstein (*110*) uses 2-anthraquinone sulfonate to identify morphine and codeine. Reimers (*315*) identifies barbituric acid, benzoic acid, and sulfonamide derivatives by refractive indices of the melt. West and Granatelli (*380*) use 8-quinolinol as a fusion reagent to give precipitates characteristic of inorganic ions.

Gettler, Umberger, and Goldbaum (*139*) report a very neat method of sublimation onto a vertical film in a temperature gradient so that the condensates are separated into zones.

PHASE CONTRAST

A comprehensive text, "Phase Microscopy" by Bennett, Osterberg, Jupnik, and Richards (*40*) has been published. Other general studies such as Richter (*324*), Tanfield and Hughes (*363*), Richards (*318*), and Osterberg (*297*) may also help the microscopist to understand and use this new tool.

The theory of phase contrast has been investigated by Zernicke (*410*), who discusses a precision method for determining small phase differences; by Di Francia (*94*); Epstein (*104*); Françon (*118, 132*), who discusses the theoretical resolving power of phase contrast optics; by Osterberg (*296*), the multipupil in phase microscopy; by Keck and Brice (*192*), image contrast in phase microscopy; and by Epstein (*105*), the edge effect in phase contrast.

Françon (*118–132*) has reported a number of unique ideas to improve contrast, resolving power, and numerical aperture. Among these are a method using uniaxial crystal plates to separate two images for interference study (*121*), a Savart polariscope between object and objective to double the contrast obtained with usual phase (*119*), phase contrast units for use with an ordinary microscope (*131*), and a phase contrast unit placed between object and objective which can be used for oil immersion or lower N.A. objectives (*123*), a variable phase plate (by reflection) which replaces the usual eyepiece (*130*), and a phase contrast accessory separate from the microscope using a phase plate of variable absorption (*129*).

The use of polarized light in conjunction with phase contrast is discussed by Kastler and Montarnal (*191*) and by Montamal (*282*); and variable phase is discussed by Nakamura and Kubota (*287*) and Osterberg and Pride (*300*). Phase contrast and color is covered by Saylor, Brice, and Zernike (*340*), Barer (*24*), and Wolter (*396*). The combination of phase contrast and interference contrast is also discussed by Barer (*26*). Wolter (*395*) compares phase contrast, dark field, and schlieren methods.

The applications of phase contrast are covered by a number of investigations: for metals and other opaque surfaces by reflection (*39, 78, 87, 106, 189, 270, 304, 351*), mineralogy and petrography (*352, 353*), monomolecular films (*127*), cylindrical and spherical transparent objects (*135, 284*), polished glass surfaces (*313*) and biological problems (*23, 306, 307, 316, 319, 377*). Finally, Crossmon (*85*) has published a discussion on the choice of mounting media for phase contrast.

FLUORESCENCE MICROSCOPY

The use of fluorescence is becoming more and more useful especially in biology. Two new texts, "Beiträge zur Fluoreszenz-Mikroscopie" (*61*) and "Fluoreszenz-Mikroscopie und Mikrobiologie" (*361*); several general studies contain useful information: Meisel (*271*) and Strugger (*362*). Other studies on practical matters such as immersion media (*92*), liquid fluorescent screens (*19*), high pressure mercury source (*196*), and a comparison of absorption and emission spectra of thioflavine-S and auramine (*230*) have also appeared. Brumberg (*63*) has described a fluorescent microscope in which the image formed by ultraviolet light on a fluorescent screen is examined with a second microscope.

Some of the applications of fluorescent microscopy are to the tanning industry (*88*), the examination of wood tissues (*266*), the study of chlorophyll in algae (*365*), and the study of minerals (*403*).

ULTRAVIOLET MICROSCOPY

This subject differs from fluorescence microscopy in that ultraviolet light is used for differentiation of specimen detail rather than for greater resolving power. The most interesting development in this field is the possibility of a color translating ultraviolet microscope (*52, 220*). The use of ultraviolet phase microscopy is discussed by Bennett *et al.* (*41*), and both Foster and Thiel (*117*) and Johnson (*186, 187*) discuss achromatic ultraviolet objectives. The application of ultraviolet microscopy to single cell studies in biology is discussed by Ludford *et al.* (*237*) and by Mellors *et al.* (*275*). Brumberg *et al.* (*64*) have reported on the etching of metals and minerals for ultraviolet examination.

INFRARED MICROSCOPY

This section includes references on reflection objectives, infrared microspectroscopy, and the use of infrared illumination in microscopy through use of image converters.

The principal advantage of reflection objectives, their achromaticity, is only slightly more important than the fact that they can be used at any wave length from far ultraviolet to far infrared since they have no refracting and therefore absorbing elements.

They are also generally characterized by a long working distance. Drew (*98*) reports a 1-cm. working distance for an N.A. = 0.6 objective. Johnson (*186*) and others (*280, 292, 293*) also report special reflection objectives. Mellors (*274*) has published a discussion on reflecting microscopes. The application of the reflecting microscope to special problems such as examination of nuclear track plates (*35*), and ceramic surfaces (*347*), where the long working distance is essential, has been described.

The application of reflection optics to spectroscopy, whereby infrared absorption patterns from micro samples (single crystals, fibers) can be obtained, has developed within the last five years (*51, 234*). Equipment designs and applications of this new tool are discussed (*29, 30, 77, 115, 145*).

Bailly (*21*) has proposed the use of an image converter tube such as that developed for use in the snooperscope for converting an infrared image to a visible one. In this way, many substances ordinarily opaque in the visible can be examined by transmitted light. Such an instrument is described by McCrone and Perrine (*260*) and by Foster (*115*), and its application to the study of the optical properties of potassium permanganate is described by McCrone (*244*).

DIFFRACTION MICROSCOPY

This section covers the newly proposed microscopy by reconstructed wave-fronts. It is feasible to achieve a resolution of 1 A. in two stages. In the first stage the object is illuminated with a coherent monochromatic wave, and the diffraction pattern resulting from interference of the coherent secondary wave from the object with the strong coherent background is recorded on a photographic plate. In the second stage this plate, after suitable processing, is replaced in the original position and illuminated with the coherent background alone. An enlarged image of the object then appears behind the plate in the original position.

The theory behind this potentially powerful technique has been discussed principally by Gabor (*136, 137, 138*). Haine and coworkers (*159–161*) and Rogers (*330, 331*) have also reviewed the theory and Bragg (*58*) has presented a simplified treatment of the theory. Baez (*20*) has discussed the use of this technique with respect to x-rays and Buerger (*67, 68*) has shown single atoms by using x-rays in the first stage.

ION MICROSCOPY

Müller's work on the field emission microscope has apparently generated considerable interest in this field. Weiser (*378*) has published details of construction of a simple field emission microscope giving magnifications of about 1,000,000 ×. A review of the entire field by Ashworth (*18*) has appeared. Müller himself has reported (*285*) that by reversing the field positive ions become the image forming radiation and increased resolving power is obtained.

Boersch (*53*) has built an ion microscope using lithium ions, Sasaki's (*338*) ion microscope has a transverse magnetic field. Magnan (*262*) and Chanson and Magnan (*72*) report a magnification of 25,000 using a new proton microscope.

INTERFERENCE MICROSCOPY

The interference microscope has developed during the past few years to the point where differences of a few angstroms in vertical height on a surface or minute differences in optical path can be measured.

Wolter (*399*) has described a simple conversion of an ordinary microscope to an interference microscope. A number of specialized interference microscopes have been described (*100, 120, 125, 126, 217, 218, 272, 339*). Barer (*28*) has projected the light from the interference microscope on to the entrance slit of a spectrograph for closer study of phase differences and absorption properties.

Rahbek and Omar (*314*) measure the thickness of thin films, Tolansky and Omar (*368*), Kohaut (*207*), Dyson (*100*), and Krug and Lau (*218*) measure surface topography; Tolansky and Omar (*368*) use the simple expedient of interference from top and bottom surfaces of a thin film of Canada balsam evaporated onto the surface under study.

Studies of absorbance of transparent materials such as glass, and plastics (*2, 108, 398*) and of cells in biological specimens (*27, 90, 103*) have been reported. Françon (*124*) has compared the results obtained by interference microscopy and phase contrast and concludes the latter is more sensitive.

X-RAY MICROSCOPY

The x-ray microscope is not yet a commercial instrument although considerable progress has been made (*34*). There are two general types: The x-ray shadow microscope which will never be a high resolving power system but which has shown some excellent results at low magnification of 100 to 200 × (*79, 80, 177*); and the x-ray focusing system which has been the subject of much work by Kirkpatrick (*197, 198*), Lucht and Harker (*236*), Wilsdorf (*392*), and Ramachandran (*311, 312*).

Farrant (*107*) has discussed the advantages of soft x-rays in x-ray microscopy and a number of investigations have appeared on the theoretical and practical resolving power of the x-ray microscope (*101, 178, 198, 309*).

TV MICROSCOPY

The ultimate in the application of electronics to microscopy has been reached in the application of a television camera, transmitter, and receiver to viewing a microscopical image. Not only does this enhance the possibilities of microprojection to large audiences (*411, 412*), but it permits incredibly rapid electronic counting and measurement in particulate systems (*325, 326, 404*).

METALLOGRAPHY

A few references in this field are of general interest to chemical microscopists. Bishop (*50*) reports a new type of metallurgical microscope, and Long (*233*) discusses a high temperature reflecting microscope for metallographic work developed by Dewhirst and Olney. The microscopic detection of overheating and burning of steel is discussed by Preece and Nutting (*308*) and a magnetic method for microscopic examination of austenitic steels by Bergh (*48*). This latter scheme effectively "stains" ferromagnetic constituents by applying a dilute suspension of very fine magnetic particles.

A symposium on titanium covered the metallography of that metal (*258*). Neuerberg (*288*) has extended his study of the optical properties of opaque materials in polarized light with an investigation of the effect of rotation of the objectives on such properties.

BIOLOGICAL APPLICATIONS

A new edition of the "Handbook of Microscopical Technique for Workers in Animal and Plant Tissue" has appeared (*188*). The use of the ultraviolet microscope in biology is discussed by Taylor (*364*). Three new devices to make life easier for biologists are described: a low-power micromanipulator and microdissector (*31*), a foot-focusing device for binocular dissecting microscopes (*276*), and a stage for continuous anaesthetization of insects (*391*).

Studies of nerve fibers (*229*), and of fibrin and fibrinogen (*162*) are reported as well as the use of the polarizing microscope for the study of crystalline viruses in tobacco (*387*). The use of polarized light in botanical cytology is discussed generally by Pfeiffer (*305*). The microspectroscopy of living and fixed cells is reported by Mellors (*273*) and Glick, Engstrom, and Malmstrom (*143*) discuss the factors affecting infrared and ultraviolet microspectroscopy and x-ray absorption in the study of cell structure.

SURFACES

The study of surfaces by the oblique-section technique is covered by Klemm (*199*). Tolansky (*367*), by placing a fine wire at the field diaphragm of a high resolving power metallurgical microscope and using an off-center incident illuminating pencil of light, achieves resolution of 0.25 micron detail in depth or extension. Tolansky and Omar (*369*) also use a light profile microscope to evaluate small radii of curvature, and Mather (*268*) recommends the preparation of high-contrast surface replicas by pressure contact on photographic emulsions.

RESINOGRAPHY AND FRACTOGRAPHY

Rochow and coworkers (*327, 328*) have continued to apply this technique to plastics and especially to the study of fillers. Zappfe *et al.* (*405, 406*) and Zednik and Kaderavek (*407*) have extended the applications of fractography in the study of metal fractures.

FIBER MICROSCOPY

Several general texts and papers have appeared recently, among them are Herzog's "Handbuch der Mikroskopischen Technik für Fasertechnologen" (*175*) and studies by Royer and Maresh (*336*), Wildman and Appleyard (*385*), and Morehead (*284*) who discusses light, electron, and phase microscopy in fiber study. Hall (*163*) has published a book, "Identification of Textile Materials," and two studies have appeared on the preparation of microscopic fiber preparations—one on the use of pectic enzymes for chemical maceration of fibers (*176*) and one on a permanent mountant (*62*). A method of longitudinal sectioning of cords and fabrics has been reported by Davis (*91*).

The cotton fiber has been studied by Rollins and coworkers (*70, 283, 371*) and wool by Rodman and Pansey (*329*) and Algera (*1*). The effect of beating on fiber structure is the subject of a study by Widerkehr (*383*) and Royer (*334, 335*), and Millson and Turl (*278*) have studied the dyeing of fibers microscopically.

PARTICLE SIZE

The collection of microscopic samples of dust is discussed by Paxton (*302*), Hurtig and Perry (*181*) who use coated slides or plates, and by Tervet *et al.* (*366*) who use a cyclone-type collector. Three authors have used the ultramicroscope to study fine particles in lyogels (*172*), industrial dusts (*36*), and colloids (*346*).

Frechette (*133*) uses a drawing camera and external scale to measure particle size. Helml and Schedling (*174*) have investigated the error in measurement of diameter of selenium particles as a function of diameter, and Schedling (*342*) has studied the correction to be applied to observed particle size measurements by measuring the over-all dimension of two particles in contact. Hawksley (*173*) has described in detail the limitations to the microscopic method of particle size determination for particles under 2 microns.

Leary (*228*) has measured the particle size of radioactive particles by counting the nuclear tracks in a radioautograph emulsion, and Wilchinsky (*384*) uses microscopic methods to standardize the Roller elutriator for measurement of catalyst particle size.

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Raman Spectroscopy

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THE last review on Raman effect in this series appeared in January 1950 (*14*). However, the publication of other very good surveys (*2, 9, 105, 126, 140, 141*), two books (*59, 124*), and a bibliography (*3*) has made it unnecessary to list all the articles since 1950. Consequently, the present compilation includes papers published from October 1952 to October 1953. (Several exceptions will be noted.)

THEORY

There are nine publications listed which are concerned with the subject of intensities (*10, 26, 67, 92, 101, 174, 191–193*). Of these, one by Long (*92*) reviews the theories and presents a matrix method for calculating derived invariants of α (polarizability) in terms of α functions characteristic of bonds and normal modes, and another by Theimer (*174*) provides extensive tables pertaining to the vibrations permitted in all the various point groups normally encountered.

There are fourteen publications which have something in common, inasmuch as they employ previously published data for testing the theoretical aspects of interaction of vibration-rotation (*47*), improvements in methods of calculating force constants (*93, 176, 180, 194*), applications of group theory (*46*), internal rotation (*106, 107*), torsional vibrations (*170–172*), a viewpoint on the true meaning of the term "characteristic frequency" (*110*), the effect of electronic arrangement on certain vibration frequencies (*142*), and the use of statistical theory in interpreting ρ data (*178*).

Davies (*30*) and Matossi (*100*) have extended the basic theories of polarizability; Stein (*162*) has calculated values of α for paraffins from bond α's; and Stansbury *et al.* (*160*) give values of ($\partial\alpha/\partial q$) determined from intensity ratios (Raman/Rayleigh) in the gas state (hydrogen, deuterium, hydrogen bromide, nitrogen, oxygen, carbon dioxide, and methane).

MOLECULAR STRUCTURE

There are 54 publications in this field (*5, 8, 18, 22, 24, 32, 35, 36, 38–45, 48, 49, 52–56, 60, 61, 64, 70, 75, 87, 91, 94, 97, 98, 102, 104, 109, 118–122, 127, 128, 132, 134, 143, 144, 150, 151, 163, 164, 177, 186*), nearly all concerned with infrared and Raman spectra, vibrational analysis, and assignment of frequencies. In addition, some contain the calculated values of the thermodynamic functions in the ideal gas state. [See (*95*) for values on cyanogen fluoride.] The subject matter can generally be inferred from the titles in the bibliography.

Of the 25 papers (*19–21, 25, 31, 50, 51, 73, 80–82, 84–86, 99, 116, 117, 123, 125, 131, 139, 152, 153, 183, 190*) dealing with crystals, the majority consist of contributions from India and France; five (*73, 117, 152, 183, 190*) are concerned with the theory of lattice vibrations.

New and finer details in the Raman spectra of gases have been obtained in Canada. The molecules studied are ammonia (*28*), ethylene (*27, 166*), benzene (*167*), and methane, methyl chloride, methylene chloride, chloroform, and methyl bromide (*187*). The techniques employed are discussed under Apparatus. To the reviewer, the photographing of the rotational Raman spectrum of benzene vapor (*167*) ($B_0 = 0.18955$ cm.$^{-1}$, $D_0 = 1.2 \times 10^{-8}$ cm.$^{-1}$, and $I_0 = 147.64 \times 10^{-40}$ gram × cm.^{2}) indicates that we have passed a very important milestone in this particular field.

As in the past, the method has continued to give worth-while information about geometrical isomerism (*6, 29, 58, 112*) and rotational isomerism (*7, 74, 108, 115, 133, 195*). (The last three papers are concerned with a mild controversy over the structure of oxalyl chloride.)

MISCELLANEOUS APPLICATIONS

Vibrational spectra are useful in obtaining evidence of inter- and intramolecular association. Of the ten papers listed here, seven (*37, 66, 129, 130, 135, 146, 168*) give results on a variety of systems, and three (*137, 138, 189*) on the heat of mixing of acetone and saturated hydrocarbons.

Three papers (*62, 63, 83*) discuss the Raman spectra of glasses. In one of these (*83*) the relative scattering powers of fused quartz and pure ether have been compared (I quartz $\sim 28\%$ I ether), and the Doppler components observed for transverse and background scattering (2537 A.) have been found to agree with values calculated from known elastic constants.

The spectra of many compounds are obtained and are never interpreted completely; also, spectra are obtained of products resulting from chemical preparations. In these categories are two articles (*158, 179*) on inorganic compounds (for bromine monochloride, chlorine and bromine, ν = 428, 551, and 313 cm.$^{-1}$, respectively) (*158*), five on miscellaneous silicohydrocarbons (*79, 113, 114, 136, 185*), and fifteen (*16, 57, 65, 68, 88–90, 111, 148, 149, 161, 173, 175, 181, 184*) on miscellaneous organic compounds.

APPARATUS, ACCESSORIES, AND TECHNIQUES

The techniques used for gases (*27, 28, 166, 167, 187*) have originated for the most part at the University of Toronto under the guidance of Crawford and Welsh, although Nielsen and coworkers (*23*) at the University of Oklahoma have also made significant contributions. The work by Stoichiff on benzene (*167*) employed all the present-day (and older) techniques: intense Toronto-type arcs (*187*), multiple-reflection sample tube (*188*), a 1 to 3 image slicer between the sample tube and the slit, and a cylindrical lens in front of the plate to increase the brilliance of the image of the line.

For illuminating single crystals the exposure time was cut from 40 hours to 1 hour by placing the crystal at the common foci of two ellipsoids and quartz mercury arcs at the other two foci (*82*). Brandmüller (*11*) has employed multilayer interference filters in a technique for photographing spectra of crystal powders, and a new liquid filter solution of 20% $[Cu(NH_3)_4]SO_4$ containing 4 grams of ammonium bromide per 20 ml. of solution for suppressing the continuous background has been announced by Simon and Jentzsch (*145*).

Two studies (*71, 76*) of mercury arc sources have shown that the greatest stability will occur at a temperature of 50°C. The helium source has been used again by Stammreich (*157–159*) for studying colored substances.

Barredo (*4*) has described apparatus for ρ measurements at low temperatures, and Singh (*147*) has found small but definite effects produced in Raman and Rayleigh scattering by application of a strong electrostatic field.

The earlier work by Rank and collaborators (see *126* for references) has led to further developments in photoelectric Raman spectrometers. We find three papers from Germany (*12, 13, 96*), one from France (*33*), one from Sweden (*78*) (an extensive bibliography and other useful information), and four from the United States (*15, 17, 154, 155*). The fundamental principles involved in the design of such instruments have been discussed (*15, 17, 69, 155, 156*).

ANALYTICAL APPLICATIONS

There are eight papers (*1, 34, 72, 77, 103, 145, 169, 182*) and one book (*124*) in this category. It was found (*34, 103*) that the intensity ratios of line pairs were proportional to concentration ratios for both nonassociated and associated systems, except that in the latter it is necessary to work with Raman lines attributable to vibrations of atoms not directly involved in association. (These generalizations apply only to the systems studied.)

Sushchinskiĭ (*169*) has described a method of analysis involving a quantity called the width of the Raman line and defined by $\delta = I_\infty/I_0$, the ratio of integrated intensity to peak intensity. In this scheme, the widths of the 801 cm.$^{-1}$ line of cyclohexane and the 992 cm.$^{-1}$ of benzene are taken as δ = 1.9 cm.$^{-1}$ and 1.8 cm.$^{-1}$, respectively, from measurements made interferometrically by Sterin (*165*). The I_0 scale is based on 801 cm.$^{-1}$ of cyclohexane and 992 cm.$^{-1}$ of benzene having values of 250 and 1260, respectively.

Continued improvements in photoelectric spectrometers should cause a marked increase in applications of Raman effect, particularly along analytical lines.

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Emission Spectroscopy

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THE principal advances in fundamental research and applications of atomic emission spectroscopy during six postwar years, 1946–51, were reviewed in three previous reports (*87–89*). The interest in those reviews encouraged the preparation of this one covering the years 1952–53. As before, new information is listed under standard wave lengths, spectral line intensities, Zeeman effect, term analysis, hyperfine structure, isotope shifts, spectrochemical analysis, and related topics.

STANDARD WAVE LENGTHS

It was suggested 127 years ago that a wave length of light might serve as an ultimate standard of length. There is hope that this may come to pass eventually. In September 1953, an international Advisory Committee for the Definition of the Meter convened at the International Bureau of Weights and Measures in Sèvres, France. It was decided that the time has come to favor the establishment of a new definition of the meter based upon a wave length of light, in order to give the fundamental unit of length not only greater precision but also the characteristics of universality and indestructibility. This committee recommended that the meter be defined by a wave length in vacuum from an atom which has a spectrum free from hyperfine structure and all other disturbing influences. Because the committee felt that it did not have sufficient information to choose a standard radiation it suggested that certain laboratories pursue further work that may determine such a choice.

In previous reviews (*88, 89*) it was mentioned that artificial mercury-198, manufactured by transmuting gold, had supplied a new and finer ultimate standard of length than the red radiation of natural cadmium. German metrologists (*78*) have nominated krypton-84 as a candidate for this honor, and Soviet scientists (*9*) have recently proposed that red radiation from enriched cadmium-114 be the unit of length.

Comparisons of wave-length standards from Hg^{198} lamps show a reproducibility of ±0.00005 A., or ±1 part in 10^8, according to Barrell (*7*). Relative wave lengths and energy levels of Hg^{198} and Hg^{202} were accurately measured by Burns and Adams (*23*), who then did the same (*24*) for Hg^{199} and Hg^{200}.

Vacuum wave lengths ranging from 3555.3204 to 6539.9183 A. were measured for 84 argon radiations relative to red cadmium with two different reflection echelon interferometers by Littlefield and Turnbull (*82*). At this point the writer wishes to mention the possibility that natural argon-40 might conceivably be a source of the ultimate standard of length; it comprises nearly 1% of the earth's atmosphere, and requires only the development of an atomic beam lamp to produce lines practically free from Doppler widening.

Because standard wave lengths must be free from disturbing effects to be highly reproducible, the effect of some argon gas in Hg^{198} lamps was investigated by Barrell (*7*) and by Meggers and Bozman (*92*). The former measured wave lengths emitted by Hg^{198} lamps containing 3, 5, or 10 mm. (of mercury) of argon, and the latter did likewise with lamps containing 2 or 16 mm. of argon. Both agree that the wave length of the green radiation 5461 A. from mercury increases about 0.0001 A. per millimeter of argon.

The change in wave length of krypton lines as a function of gas pressure was investigated by Kosters and Engelhard (*78*). The pressure effects of argon or helium on the resonance lines of silver were investigated in absorption up to 83 atmospheres (*28*); changes in wave length were found to be linear with relative density of gas, but they increase with argon and decrease with helium and are strongly dependent on the total angular momentum of the silver atoms in excited states. The dependence of perturbing effects of foreign gases upon *J*-values was not predicted by theory of pressure shifts.

INTENSITIES

In astrophysics the determination of temperatures, relative abundance of elements, and interpretation of forbidden spectral lines rests heavily on atomic transition probabilities, oscillator strengths, or intensities of the observed spectral lines. Recent experiments to determine absolute oscillator strengths are represented by the work of Estabrook (*40*) on chromium, the results of Huldt and Lagerqvist (*62*) on chromium and manganese observed in flame spectra, and of Kopfermann and Wessel (*77*) for resonance lines 3720 and 3737 A. of iron excited in an atomic beam.

Quantum-mechanical calculations have been made of line strengths for oxygen II, neon II, sulfur II, and argon II spectra (*49*), for calcium II lines (*54, 139*), and for the sharp and diffuse series of neutral potassium (*141*). The last mentioned calculations, performed with an IBM calculator wired to compute wave functions and transition probabilities, were inspired by studies of energy distribution during a combustion process. Such calculations are greatly desired for fundamental research in complex spectra but are generally too expensive for civilian laboratories. The last review (*89*) neglected to mention that the most complete compilation of experimental and theoretical spectral-line intensities appears in the well-known "Landolt-Börnstein" (*80*).

A new record in radiometry appears to have been set by Watanabe and Inn (*143*), who measured the intensities of lines in the principal series of helium from 584 to 516 A. with a thermocouple.

ZEEMAN EFFECT

There have not been any recent observations of Zeeman effect, but a number of important papers based mainly on prewar investigations have been published: measurements of the Zeeman effect in manganese I from 2460 to 4825 A. (*26*), asymmetries of Zeeman patterns and *g*-values in manganese I (*25*), measurement of nearly 1000 patterns in rhenium spectra (*93*), a second paper on Zeeman effect and structure in tantalum I (*11*), measurement of Zeeman patterns for 540 ruthenium spark lines (*94*) photographed in 1940, Zeeman effects in four spectra of tellurium (*53*) from spectrograms made in 1936, Zeeman effect in chromium I (*73*) and chromium II (*74*), and first Zeeman data for dysprosium II (*13*) observed in 1940.

FORBIDDEN LINES

Although atomic spectra, in general, obey simple selection rules that govern transitions between atomic energy levels, "forbidden lines" are occasionally detected under special circumstances. In the case of cadmium a comparison of line intensities from enriched isotope samples proves (*58*) that the observed forbidden lines arise from the nuclear magnetic moment of an isotope having odd integral mass. A preliminary report of this was reviewed in 1950 (*88*).

A new examination of the palladium arc spectrum resulted (*126*) in the discovery of a new type of forbidden transition explained by the theory of "forced" dipole radiation, a type of Stark effect which is due to the interionic fields in the arc and causes a sharing of parity of atomic levels.

TERM ANALYSIS

The critical compilation and publication of "Atomic Energy Levels" was mentioned in previous reviews (*87–89*). This project was begun in 1946 with the object of publishing at intervals of about 3 years a series of volumes containing all available information regarding atomic energy levels derived from the analysis of optical spectra. Such information includes relative energy levels, spectral terms, quantum numbers, magnetic splitting factors, electron configurations, and ionization potentials.

Volume I, containing data from 205 spectra characteristic of the first 23 atomic numbers (1H to 23V) was published in 1949. Volume II, presenting similar data from 152 spectra of 18 elements (24Cr to 41Nb) was published in 1952 (*100*). Volume III of this series is now being prepared; it will collect all available atomic data for 34 elements (42Mo to 57La, and 72Hf to 89Ac). The fourth and final volume will deal with the two groups of rare earth elements (58Ce to 71Lu and 90Th to 98Cf) most of which are still inadequately investigated spectroscopically.

Recent publications on spectral structure are noted below; in many cases the new data on atomic energy levels were supplied in advance of publication for inclusion in the first two volumes of "Atomic Energy Levels." New wave lengths and term tables for spectra of the He I isoelectronic sequence—namely, beryllium III, boron IV, carbon V, oxygen VII, and fluorine VIII have been published by Edlén (*37*). Similar data from extreme ultraviolet arc spectra of boron, indium, thallium, lead, and bismuth were published by Clearman (*29*). Photographic infrared observations have revealed (*95*) many new lines and some new energy levels of gallium I, indium I, and thallium I. Further infrared observations with lead sulfide detectors have recorded new lines in the spectra of argon (*64*), magnesium (*42*), and lanthanum (*39*). A thermocouple was used by Humphreys (*63*) to detect at 12.37 microns the first line of the sixth series of hydrogen.

Essentially complete descriptions and analyses of the first two spectra of chromium have been recently published by Kiess (*73, 74*). These papers give full details on more than 1800 chromium II lines, and on 4400 chromium I lines; they are excellent examples of thorough and reliable investigations. The spectral terms identified with the low even configurations of molybdenum I have been reported by Trees and Harvey (*138*). The analysis of the second spectrum of manganese has been extended to 1100 classified lines (*33*), and new terms have been found in the second spectrum of iron (*120*).

A second paper on the first spectrum of tantalum has appeared (*11*), and an extension of the second spectrum of zirconium in the infrared has been reported (*72*). Primarily for purposes of analysis, entirely new descriptions of the arc and spark spectra of rhenium, comprising about 4200 rhenium I, and 1800 rhenium II lines, were published by Meggers (*90*). A paper on a single intersystem transition in the first spectrum of beryllium gave the connection between singlet and triplet terms and reported (*14*) the measured intensity ratio of beryllium resonance lines as 3×10^7.

The only recent contribution to regularities in the spectra of rare earth elements is a report (*13*) on four recurring intervals between dysprosium II lines whose Zeeman patterns indicate that the low energy levels belong to ^{6}I and ^{4}I terms, among which $^6\mathrm{I}_{81/2}$ from $4f^{10}\ 6s^1$ probably represents the ground state of Dy^+. Despite the fact that few physicists are now engaged with fine-structure analyses of atomic spectra, there is occasionally duplication of effort. Thus, identical intervals of the ($4\mathrm{S}^0$) $3p\ ^3\mathrm{P}$ term of oxygen I have been measured interferometrically by Parker and Holmes (*115*), and by Davis and Meissner (*34*).

HYPERFINE STRUCTURE

The publications mentioned under term analysis deal only with the fine structures of atomic spectra, excluding hyperfine structures and isotope shifts arising from interaction between optical electrons and atomic nuclei. However, these interactions yield highly quantitative information about certain properties of atomic nuclei and these will surely continue to be investigated so long as a satisfactory theory of nuclear structure is still lacking.

Hyperfine structures occur only with nuclei possessing magnetic properties, and when resolved, measured, and interpreted, they give numerical values to the mechanical (I), magnetic (μ), and electric quadrupole (Q) moments of the nuclei. A fairly complete compilation of these data has been supplied by Klinkenberg (*76*). Here reference will be made only to contributions from optical spectroscopy published during the past two years. Hyperfine structures of the resonance lines indicate (*70*) that $\mu = +0.136$ nuclear magneton for Au^{197}. For Pd^{105} hyperfine structure discloses (*130*) that $I = 5/2(h/2\pi)$ and $\mu = -0.57$ nuclear magneton. Both Ir^{191} and Ir^{193} have $I = 3/2\ (h/2\pi)$, and for Ir^{193} $\mu = +0.17$ nuclear magneton and $Q = +1.0$ barn (1 barn $= 10^{-24}$ square centimeter) (*108*). Resolved hyperfine structure of arsenic II lines gives for As^{75}: $\mu = 1.45$ nuclear magnetons and $Q = 0.32$ barn (*110*). From hyperfine structure in antimony spectra values of $Q = -1.3$ barn, and -1.7 barn have been derived for Sb^{121} and Sb^{123} respectively (*129*). Results reported for Ta^{181} are $\mu = 2.1$ nuclear magnetons and $Q = +6.5$ barn (*20*). A final report (*71*) on nuclear moments of Tc^{99} confirms that $\mathrm{I} = 9/2(h/2\pi)$, $\mu = 5.5 \pm 0.3$ nuclear magnetons, and indicates that $Q = +0.34 \pm 0.17$ barn.

The fact that no more than six components are found in many Am^{241} lines proves that $I = 5/2(h/2\pi)$ for that nucleus (*44*). The hyperfine structure of the resonance lines of indium has been completely resolved finally with an atomic beam source (*36*); the high spectroscopic accuracy led to values of the hyperfine structure splittings of the $5\ ^2\mathrm{P}_{1/2,\ 3/2}$ terms which agree within $\pm 0.0004\ K$ with microwave measurements.

In rare earth spectra, partially resolved hyperfine structure of gadolinium lines suggests that for Gd^{155} and Gd^{157} $I \leqslant 3/2\ (h/2\pi)$, $\mu \sim 0.25$ nuclear magneton for Gd^{155} and $\mu \sim 0.3$ for Gd^{157} (*136*). Likewise partially resolved hyperfine structure of dysprosium lines suggests that for Dy^{161} and Dy^{163} probably $I = 7/2(h/2\pi)$, and their nuclear magnetic moments are approximately equal (*107*). In that paper the eccentricities of odd-proton nuclei, calculated from all existing Q data, are plotted *vs.* the proton number; they appear to attain large values in certain light and heavy elements but the significance of this is not understood. The correlation of nuclear properties with nuclear structures and forces is still incomplete. A summary of 22 outstanding problem nuclei—that is, those naturally occurring isotopes for which the nuclear moments are uncertain or unknown—has been given by McNally (*83*).

ISOTOPE SHIFTS

Most natural elements consist of a mixture of two to 10 isotopes, and the different isotopes of any given element emit slightly different spectra whose separations are measured as isotope shifts. Many such measurements were referred to earlier (*87–89*), and a complete compilation of quantitative data on hyperfine structure and isotope shifts which accumulated up to 1951 was published in "Landolt-Bornstein" (*81*). Only recent (1951–1953) literature on isotope shifts is cited here. Details of experimental procedure and results are omitted, and only the isotopes for which spectral shifts have been measured are listed. These are: He^3, He^4 (*45*); Li^6, Li^7 (*61*); O^{16}, O^{18} (*114*); Mg^{24}, Mg^{25}, Mg^{26} (*104*); Mo^{95} Mo^{97} (*130*); Pd^{106}, Pd^{108}, Pd^{110} (*130*); Te^{123}, Te^{125} (*118*); Eu^{151}, Eu^{153} (*16*); Gd^{156}, Gd^{158}, Gd^{160} (*16, 18, 134*); Er^{164}, Er^{166}, Er^{168}, Er^{170} (*109, 145*); Yb^{170}, Yb^{171}, Yb^{172}, Yb^{173}, Yb^{174}, Yb^{176} (*16, 111*); W^{182}, W^{184}, W^{186} (*105*); Os^{186}, Os^{188}, Os^{190}, Os^{192} (*135*); Pb^{204}, Pb^{206}, Pb^{207}, Pb^{208}, Pb^{210} (*17, 106, 131*); Th^{230}, Th^{232} (*132*); U^{233}, U^{234}, U^{235}, U^{236}, U^{238} (*127*); Pu^{238}, Pu^{239}, Pu^{240}, Pu^{242} (*30*).

Although the centers of gravity of spectral terms of different isotopes of an element are usually relatively displaced, the interpretation of these shifts is still far from satisfactory. For light elements this isotope shift is generally explained as a "nuclear mass effect," whereas for heavy elements it is usually ascribed to a "nuclear volume effect." In the latter cases, for more than two isotopes, the term centers of gravity are often not equidistant. Some of these irregularities are blamed on perturbations and others on "magic numbers." Attention has been called (*17*) to the fact that isotope shifts show a discontinuity for closed shells of 50, 82, and 126 neutrons.

The isotope shifts for elements of intermediate weight have not been discussed in detail. Coming from many different sources and measured with various degrees of accuracy, the reported isotope shifts leave something to be desired in homogeneity and precision. In some spectra isotope shifts have been measured for only one or two lines while in others for several hundred. In at least two cases (*105*, *145*) claims were made that it is possible with the aid of isotope shifts to differentiate electron configurations, thus offering hope that in the future they may aid in the fine-structure analysis of complex spectra, as well as in clarification of nuclear physics. Most of the recent researches on hyperfine structures and isotope shifts have been performed by the demilitarized Germans and Japanese.

In the preceding review (*89*) the creation of a Joint Commission for Spectroscopy was mentioned. That commission was organized to collect information on spectroscopic research, equipment, results, and problems of mutual interest to the International Union for Pure and Applied Physics and to the International Astronomical Union. At its Rome meeting in September 1952, the Joint Commission for Spectroscopy received provisional reports of Subcommittees on Institutes and Equipment, Atomic Spectra, Spectra of Diatomic Molecules, Spectra of Polyatomic Molecules, Notation for Atomic Spectra, Notation for Spectra of Diatomic Molecules, and Exchange of Research Problems. These reports, along with minutes of the Rome Meeting, have been published as Transactions of the Joint Commission for Spectroscopy (*137*); they should be read by all living or active spectroscopists.

Four recommendations of that commission are so important that they are quoted here:

> The Joint Commission for Spectroscopy recommends the use of the tables of Edlén for converting wave lengths in standard air to wave lengths in vacuum. Those tables are based on a new formula (*38*), $(n - 1)\ 10^7 = 643.28 + 294981(146 - \sigma^2)^{-1} + 2554.0\ (41 - \sigma^2)^{-1}$, which represents the index of refraction n of standard air with an accuracy of $\pm 1 \times 10^8$ down to 2000 A.
>
> The Joint Commission for Spectroscopy reommends the universal use of the symbol σ for wave number instead of ν, in order to avoid confusion with the frequency symbol.
>
> The Joint Commission for Spectroscopy recommends that the conversion factor for computing the energy in electron volts from wave number units (kayser) shall be 0.00012395 to conform to the standard book "Atomic Energy Levels." Various proposed values of that conversion factor made it seem desirable to advise universal use of one value.
>
> The Joint Commission for Spectroscopy recommends that the unit of wave number hitherto designated as cm.$^{-1}$ be named kayser with the natural abbreviation K. This recommendation supports the most logical proposal for a simple symbol and two-syllable word for the unit that has hitherto awkwardly been represented by cm.$^{-1}$ and clumsily called reciprocal centimeter or centimeter to the minus one.

SPECTROCHEMICAL ANALYSIS

Intensive use of atomic emission spectra for quantitative chemical analysis is scarcely 30 years old, but it has expanded with acceleration since 1925. This is shown by the "Index to the Literature of Spectrochemical Analysis" prepared by Meggers and Scribner (*96*), Part I of which listed 1482 papers from 1920 to 1939, inclusive, Part II more than 1000 papers in the interval 1940 to 1945, and Part III about 1250 papers from 1945 to 1950. Only a few from 1951 to 1953 have been here selected to illustrate interesting developments.

The publication of books dealing with spectrochemical analysis appears to be declining; in the last review (*89*) eight could be mentioned, but here only two—namely, "Metal Spectroscopy" (*140*) and "Methods for Emission Spectrochemical Analysis" (*3*). The latter represents a first approach to standardization of empirical procedures for analyzing metals, alloys, and some nonmetals, with special emphasis on exposure conditions, excitation conditions, and analytical line-pair data. Publications designed to present dependable data, "Atomic Energy Levels" (*100*) and an "Ultraviolet Multiplet Table" (*99*), are now available for spectra of atomic numbers 1 to 41, inclusive; they are in preparation for the remaining elements. The multiplet tables give excitation data for most of the spectral lines likely to be used by spectrographers.

The rapid development of the art of spectrochemical analysis has entailed an expansion in scientific language as well as in scientific literature; it has resulted in publication (*3*, *59*) of a suggested nomenclature in applied spectroscopy, including recommended definitions of technical terms that are used in the literature of spectrochemical analysis.

Since no practical absolute method of determining chemical composition by means of spectra has been devised all quantitative analyses are relative to standards. The preparation and testing of typical spectrographic standards of steel, aluminum, tin, ores, glass, and minerals has been described by Scribner and Corliss (*125*). The direct synthesis of spectrochemical standards by powder metallurgy techniques was described by Gerber (*50*) and Jaycox (*66*). Three graded series of copper standards were described by Smith (*128*).

With regard to light sources used for spectrochemistry, four improvements or variations of the interrupted direct current arc are noted (*6*, *21*, *22*, *119*); there is also an improved spark generator (*22*) and a universal spectroscopic source unit (*146*). The construction of hollow cathode sources for spectrography (*51*, *98*, *112*, *124*) and of electrodeless high-frequency sources (*32*, *69*, *147*) are described. The possibilities and limitations of these sources have not yet been fully explored, but they appear to be especially suited for gas analysis.

Noteworthy applications of spectroscopy to gas analysis are found in the determination of fluorine by means of a calcium fluoride band (*47*, *52*) in arc spectra; chlorine, bromine, and iodine in an improved hollow-cathode source (*51*); chlorine and bromine in engine deposits (*84*); chlorine in stony meteorites (*121*); oxygen in steel (*117*); nitrogen in organic compounds (*46*); deuterium in hydrogen-deuterium mixtures (*19*); and total water content of a hydrate by dissolving the sample in deuterium oxide and determining the intensities of the H_β and D_β lines in a high-frequency electrodeless discharge (*102*).

The use of photoelectric direct-reading spectrometers in metallurgical production control has become commonplace, but attention is called to two investigations (*8*, *10*) analyzing some sources of error likely in measurements made with such instruments. A new approach to direct-reading spectrochemical analysis (*15*) has been described, but it is so elaborated with electronics that it is incomprehensible to an old-fashioned spectroscopist.

Another contribution has been made (*123*) toward a description of mutual effects of certain elements on spectral-line intensities in the direct current arc. Three recent papers (*4*, *60*, *122*) deal with the sensitivity of spectral detection of impurities in lead; one reports (*4*) that the limits of detection of 14 elements range from 0.00003% silver to 0.01% tellurium, another states (*60*) that the minimum detectable silver is 0.000001%, and the third (*122*) says it is 0.001%. The disagreement is extraordinary!

In general, the routine spectrochemical analysis of metallic alloys is so accurate and quick that mention of recent applications will here be restricted to some examples in which chemical methods are impractical or wholly inapplicable. Thus the determination of hafnium in zirconium (*31*, *75*, *103*) is spectrographically simple but chemically complicated; likewise the separate determination of niobium and tantalum in stainless steel (*116*). Mixtures of rare earths are successfully analyzed (*41*, *113*) only by spectrographic methods.

For spectrochemical identification, wave lengths and estimated relative intensities of the stronger lines of artificial technetium and promethium were presented by Meggers (*91*). Although neither element has been detected terrestrially, technetium has been tentatively identified in the solar spectrum (*101*), and appears to be relatively abundant in certain stars (*97*). Spectroisotopic analysis of lithium (*133*), plutonium (*30*), and various other elements (*83*) can now be performed by resolving the isotope shifts and measuring relative intensities.

The vital importance of optics in the oil industry (*43*) is illustrated by the spectrographic determination of metallic constituents of petroleum (*48, 56, 67, 68, 86*) because some trace metals in petroleum fractions may cause deterioration of cracking catalysts, corrosion of refractories, or may promote chemical reactions resulting in lubricant breakdown and engine wear. Other trace metals are employed as additives to oils or gasolines.

After astrophysics, which is universal, the next largest domain of applied spectroscopy is geochemistry. As a tool in geochemistry (*1*) spectrochemical analysis has demonstrated that the potassium-rubidium ratio is constant in all common rock types and in meteorites (*2*), that the abundance of radioactive K^{40} in dunite is actually about $^1/_{30}$ that resulting from chemical determinations, and that the minimum age of the earth as measured by the Rb^{87}-Sr^{87} ratio is 2×10^9 years. A statistical comparison of precision of chemical and spectrographic determinations of the major constituent elements in rocks and minerals shows that the former is better for silica and alumina but the latter is superior for iron and, manganese, magnesium, calcium, sodium, and potassium oxides (*35*).

Some alluring applications of spectrochemical analysis to massive materials are found in determinations of the strontium content of limestones and fossils (*79*), trace elements in sea water and marine algae (*12*), and rare elements in coal. Thus the germanium content of some 200 British coals (*5*) and about 80 Japanese coals (*65*) has been reported, and the industrial significance of metals in coal is suggested by analyses of 596 samples for 38 elements (*57*) showing that, relative to the earth's crust, coal ash is 10 to 185 times richer in lithium, strontium, silver, arsenic, bismuth, boron, gallium, germanium, lanthanum, mercury, lead, antimony, tin, zinc, and zirconium.

Salts of the Dead Sea have been analyzed spectrographically for their rubidium content (*55*). Since silver has been found spectroscopically in normal human hair of all age groups (*142*), the expression "silvery locks" can now be applied to any normal human with hair.

A direct spectrographic method for detecting minute amounts of obnoxious beryllium in air has been devised (*27*), and applications of spectrography to criminology (*85, 144*) are illustrated by the determination of metallic paints and poisons, and the identification of safebreakers and murderers. These examples suffice to show that spectrochemical analysis not only protects our health but also improves our morals.

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Mass Spectrometry

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THE broad survey of the literature of mass spectrometry attempted in the preceding review (*61*) is continued in the present one on the premise of expanded mutual interests of chemists and physicists in the many fields of science to which mass spectrometry contributes. An effort has been made to include papers, especially of foreign origin, published too late to be included in the previous review.

Activity in mass spectrometry continues to increase in scope and intensity. Aside from the magnitude of the present review, comprehensive accounts of the theory, instrumentation, and applications of mass spectrometry (*16, 84, 160, 202, 209, 230*) attest to this fact. Other reviews (*57, 65, 149, 157, 181, 182, 191, 255, 257*) consider recent developments and applications in varying detail, stressing for the most part chemical and isotopic analysis.

INSTRUMENTATION, METHODS AND TECHNIQUES

Mattauch (*203, 204*) gives an extensive description of the various types of electrical and magnetic field arrangements used in conventional instruments for precise mass measurements. He also reports a method for determining dispersion in mass spectrography (*207*). The construction of a Mattauch-type mass spectrograph with a resolution of about 1/12,000 is reported by Delfosse and Nève de Mevergnies (*59*). Herzog (*140*) describes a new instrument with anastigmatic image which utilizes a combination of a spherical condenser and a homogeneous magnetic field. A new instrument utilizing no magnetic field is described by Paul and Steinwedel (*246*). Miller and coworkers (*212*) report the development and certain clinical applications of a portable instrument that reports the concentrations of five gases every 20 seconds with 1% accuracy.

Plumlee (*251*) describes instruments for use in electron and ion bombardment of surfaces. A number of relatively simple instruments are described (*51, 197, 213, 248*) for general chemical and isotopic analysis and for leak detection. The continued interest in radio-frequency and time-of-flight mass spectrometers which involve no magnetic field is apparent in a number of papers (*22, 113, 253, 254, 307, 337*). Recent work with timing instruments based on cyclotron resonance is also described (*147, 280*).

A surprising number of studies are specifically concerned with proper operating conditions and possible sources of error for a variety of applications of the mass spectrometer. Zemany (*339*) discusses the principles of free molecular flow in the sample inlet to the mass spectrometer, and Kistemaker (*180*) reports the influence of fractionizing and viscosity effects in the gas-handling system. A note on the necessary conditions for applying the superposition method in mass spectrometry is given by Careri (*38*).

The distribution of errors in the photometric determination of isotope abundances (*205*), corrections in abundance measurements obtained with electron multipliers (*250*), and the suppression of spurious ions from secondary negative particles (*142*) are also considered. Waldron and Wood (*321*) discuss possible sources of error and experimental techniques for eliminating the most serious ones in appearance potential measurements.

Descriptions of conventional and novel ion sources and recording systems are given by a number of authors. Barnard (*17*) gives a general discussion of ion sources using electron guns, and Vauthier (*317*) describes an electron gun that does not require an auxiliary magnetic field for collimation. Descriptions are also given of furnace sources (*37, 243, 326*) and surface ionization sources for positive ions (*5, 159*) and negative ions (*145*).

Tsukada (*310*) gives a detailed description of an oscillator-type source for use with a spiral orbit mass spectrometer. Recording systems using alternating or direct current amplification are described in which ion current is displayed on recording devices (*31, 165, 232*) or on cathode-ray tubes (*85, 314*). Stevens and Inghram (*288*) describe a modification of the ratio recording system applicable to surface ionization sources. A recording device that requires the mass spectrometer to hunt over a predetermined mass range and to "lock on" a specific ion peak is also reported (*79*). Robinson (*268*) discusses the application of a mass spectrometer to process control.

A number of papers describe specific parts of or equipment associated with a mass spectrometer. Advantages, design, and application of permanent magnets are discussed by Hadfield and Mawson (*119*). The form of the pole pieces used in the spiral orbit mass spectrometer is given by Sakai and Nogami (*271*).

Details are given for an emission regulator (*284*), a power supply for a thermionic source (*260*), a cement base for a hot filament ion source (*123*), and the control and stabilization of the magnetic field of a mass spectrometer (*322*). Berry (*25*) reports a means of obtaining high resolution in a conventional 180° instrument. An automatic device is described for the rapid determination of ionization efficiency curves (*137*).

A gas-handling system for routine isotopic analysis is reported by von Ubisch (*312*). Details of vacuum locks for solid sample introduction are given (*107, 287*). Nief (*229*) describes a simple method of making a molecular leak, whereas Babelay and Smith (*10*) have developed a needle-valve type of variable gas leak with provision for both molecular and mass flow. A simple diaphragm micromanometer utilizing capacitance measurement of the diaphragm movement is reported by Cook and Danby (*50*).

An isolation trap described by Alpert (*7*) for use between an oil diffusion pump and the mass spectrometer contains corrugated copper foil and requires no refrigerant. Reynolds (*261*) reports the successful threading of quartz and borosilicate glass rods for use as studs in mounting successive slit plates in an ion source.

ION OPTICS

Many of the references given in this section are mathematical or geometrical studies of ion sources (*296, 304*), analyses of design (*96, 110, 139, 146, 247, 256*), or discussions of the effects of various parameters on ion optics (*297*) and resolution (*176*).

The effect of space charge on focusing properties is considered in several papers (*19, 20, 320*). Angular aberration (*39, 166, 220*) and second-order focusing (*108*) are also discussed.

Two-directional focusing with uniform magnetic fields is described by Cross (*54*) and Reutersward (*258*). Fischer reports a theoretical treatment (*89*) and an experimental arrangement (*90*) of a mass spectrometer with double directional focusing and velocity focusing. Paul (*245*) gives an experimental and theoretical discussion of the effects of stray fields on the qualities of a sector magnetic field.

IONIZATION AND DISSOCIATION BY ELECTRON IMPACT

The accumulation of mass spectra of a wide variety of compounds continues as a basis for theoretical as well as practical studies. Mass spectra of the carbonyls of tungsten, iron, and nickel are reported by Baldock and Sites (*15*). Bernstein *et al.* (*24*) give the monoisotopic spectra of chlorine-substituted methanes and ethanes. Dibeler and coworkers report spectra of organometallic compounds of lead and mercury (*62*), tetramethyl compounds of carbon, silicon, germanium, tin, and lead (*60*), and of methyl siloxanes (*63*).

Henglein describes some observations with a parabola mass spectrograph on the mode of decay of ions of the type C_3H_n (*134*), the comparison of the mass spectra of singly and doubly charged hydrocarbon ions (*133, 135*), and observations of ion dissociation (*136*). Ewald and Henglein (*83*) give a brief description of the spectrum of methane obtained with a parabola instrument. Spectra of six aliphatic lactones are described by Friedman and Long (*104*). Studies of the ionization of noble gases at pressures ranging from 10^{-4} to 10^{-2} mm. of mercury are reported by Hornbeck and Molnar (*156*).

The existence of multiply charged molecule ions of the hydrogen halides is discussed by Johnston and Arnold (*170*). Mohler, Dibeler, and Reese (*214*) tabulate and discuss briefly the mass spectra of 22 fluorocarbons, including paraffins, cyclics, olefins, and polycyclics. Grundland (*117*) reports on the mass of the polymers of oxygen formed in ozonized oxygen. Gilpatrick *et al.* (*112*) describe attempts to measure the spectrum of uranium trifluoride, and Sites *et al.* (*277*) report on technetium.

The mass spectrum of the unusual molecule, butatriene, is given by Shubert (*274*). O'Neal (*240*) presents some recent work on high temperature mass spectra of hydrocarbons, and Antkiw and Dibeler (*8*) report on the mass spectra of gallium vapor. Zuk (*342*) describes a study of the ionization phenomena in air, nitrogen, oxygen, and carbon dioxide by means of a Nier-type mass spectrometer. The ionic emission of aluminosilicates is discussed by Beaussier and Couchet (*18*).

Upon consideration of accumulated mass spectral data, several authors discuss the possible theoretical basis for dissociation patterns. Magat and Viallard (*200*) conclude that no satisfactory theory covers patterns for many hydrocarbons. Rosenstock *et al.* (*269*) and Wallenstein *et al.* (*325*) discuss the mass spectra of polyatomic molecules in terms of a series of quasi-equilibrium unimolecular decompositions. The application of an absolute rate theory for such isolated systems gives results in agreement with experiments for propane.

Several papers describe some observations on ions formed by rearrangement and by secondary processes in the mass spectrometer. These include spectra of aliphatic acids (*124*), carbon dioxide (*226*), water vapor (*235*), and various hydrocarbons (*298*). Norton (*234*) discusses the formation of mercury hydride ions when mercury vapor and hydrogen gas are admitted to the mass spectrometer. Sloane (*279*) describes the liberation of positive ions by negative-ion bombardment of surfaces.

Studies of isotopic molecules form an interesting and important part of mass spectrometry. Mass spectra of deuterated isopropyl alcohols (*105*), and deuteroacetylenes, monodeuterobenzene, and deuteronaphthalenes are recently reported (*215*). Schissler, Thompson, and Turkevich (*273*) discuss the mass spectra of all of the deuteromethanes, four ethanes, and two propanes. A quantitative explanation is given of the mass spectra of the methanes. Schaeffer (*272*) compares calculated and observed spectra of some simple isotopic molecules.

Neuert (*221*) reports that the ionization potential of ammonia-d_3 is 10.72 electron volts or about 0.22 volt higher than that of ordinary ammonia. A similar effect is noted for the deuteromethanes (*188*), and Tickner, Bryce, and Lossing (*303*) point out the possible errors involved in low-voltage analyses of deuterated hydrocarbons as a result of the assumption of the same ionization potential for isotopic molecules.

Electron capture processes are discussed by Craggs, McDowell, and Warren (*52*), and negative-ion formation in gases of high dielectric strength is described by Warren, Marriott, and Craggs (*329*) and by Ahearn and Hannay (*4*). Neuert (*222*) reports a study of negative ions from the dissociation of hydrogen sulfide and selenide and the electron affinity of sulfur and selenium. Monatomic and polyatomic negative ions are reported in electric discharge studies of arsenic, phosphorus, sulfur, and thallium (*73*), and in selenium, tellurium, antimony, and bismuth (*72*). Trischka *et al.* (*308*) describe the production of negative ions at the surface of a thoriated tungsten filament.

Discussions of ionization and dissociation by electron impact are given by Stevenson (*290, 291*) and by a number of other authors (*80, 195, 216–218, 228*). Fox and coworkers (*94, 95*) continued the application of nearly monoenergic electron beams to the study of ionization probabilities and appearance potentials. They report (*93*) resolution of ionization processes associated with the $^2P_1/_2$ and $^2P_3/_2$ ground states of the ions in krypton and xenon. Bennett (*21*) and Harned and Bennett (*125*) reported measurements on ionization efficiencies of multiple ionizations in mercury by using a radio-frequency mass spectrometer.

A number of investigators report ionization and appearance potential studies of ions from a wide variety of compounds. These include: carbon monoxide, nitrogen, nitric oxide, and oxygen (*120, 121*), methane (*194*), methyl iodide (*193*), cyanogen and methyl cyanide (*196*), halogenated methanes (*34, 35, 328*), halogenated benzenes (*126*), cyclopropane (*87*), vinyl ion and radical (*88*), hydrogen sulfide, hydrogen selenide, phosphine, silane, germane (*223*), aliphatic amines (*42*), hydrogen peroxide (*267*), the CF_3 ion and radical (*64*), sterically hindered carbonium ions (*97*), and compounds containing C-S, H-S, and S-S linkages (*98*).

APPLICATION TO PHYSICAL CHEMISTRY AND CHEMICAL PHYSICS

The mass spectrometer is particularly valuable for the detection of atoms and free radicals and the identification of their reaction products. Foner and Hudson (*91*) report the identification of hydrogen, oxygen, and hydroxyl radicals in a hydrogen-oxygen flame and the methyl radical in a methane-oxygen flame. They also observed (*92*) the HO_2 radical in the gas phase reaction of hydrogen atoms and oxygen molecules. Lossing, Ingold, and Tickner, in a series of papers on free radicals in mass spectrometry, discuss the measurement of methyl radical concentration (*187*), the thermal decomposition of several oxides and ethers (*186*) and of some benzene derivatives (*162*), and the rate of combination of methyl radicals (*163, 164*).

The detection of free radicals in various heterogeneous reactions and in gaseous systems including low pressure flames is described by Le Goff (*185*), Robertson (*266*), and Taylor (*299*). Leger and Ouellet (*184*) report the use of a fast-scanning mass spectrometer for cool-flame studies that show effects with lifetimes of approximately milliseconds. Kenyon (*175*) discusses the production of and reaction of free methyl radicals with 2-chlorobutane. Zemany and Burton (*341*) report on *free radicals* in the photolysis and pyrolysis of acetaldehyde.

The mass spectrometer has also been applied to the study of the catalyzed reactions of propylene with deuterium (*30*), the exchange and hydrogenation reactions of acetylene and ethylene (*67*), the reduction of acetone (*106*), the isomerization of 1-chloropropane and the exchange of acetone and propane with deuterium (*173*), the interaction of ethylene and deuterium (*311*), and the redistribution of hydrogen during olefin hydrogenation (*319*). Studies are also reported on equilibrium in the exchange of hydrogen between phosphine and water (*332*), the exchange of oxygen-18 between oxygen gas and certain metallic oxides (*336*), the reaction of four monodeuterobutanes with concentrated sulfuric acid (*241*), and the Fischer-Tropsch reaction using deuterium gas (*302*).

A mass spectrometer utilizing molecular flow for sample introduction has been used to determine molecular weights of components in a mixture by means of Graham's law (*75*). The degree of ionic hydration of salts is also measurable (*86*) by determining the amount of oxygen-18 in carbon dioxide in equilibrium with solutions containing H_2O^{18}. Collision cross sections of negative atomic iodine ions in nitrogen and argon (*192*), ionic reactions in hydrogen (*219*), and effects at high pressures (*233*) are also discussed.

Investigations of the sublimation of graphite (*41, 154*) and of other Group IV elements (*155*) indicate the complexity of the vapors of these elements and its effect on measurements of latent heats of vaporization. Johnson *et al.* (*167*) describe a technique for determining phase transition temperatures and heats of transformation in metals.

Mass spectrometric studies of homogeneous reactions and thermal decomposition reactions are also reported. These include the discussion of a perturbation factor in the kinetics of the homogeneous protium-deuterium exchange (*28*) and a determination of the protium-tritium equilibrium (*208*). The effect of isotopes on decarboxylation (*289*) and deamination (*285*) processes and the application of deuterium in the study of the decomposition mechanisms of organic compounds (*324*) are reported. Thermal decomposition studies are also described for dioxolane (*118*) and for cyclopentane (*315*).

The thermal degradation of polymers is discussed in several papers (*2, 3, 294, 338, 340*) in which degradation occurs in an evacuated vessel with subsequent introduction of the volatile products into the mass spectrometer. A new technique is described (*33*) by which the polymer is degraded directly into the ionization chamber of the mass spectrometer permitting study of larger nonvolatile products.

ANALYTICAL APPLICATIONS

One of the major applications of the mass spectrometer is the analyses of gaseous and liquid mixtures (*9, 101, 128, 129, 144, 224, 225, 282, 316, 343*). Friedel, Sharkey, and Shultz (*100*) report the necessary conditions for accurate analyses of mixtures containing nitrogen dioxide. Hydrocarbon-type analysis is discussed by several authors (*55, 99, 189, 190*). Kinney and Cook (*177*) indicate means of identifying thiophene and benzene homologs. Meyerson (*210*) discusses the determination of benzene, cyclohexane, and methyl cyclopentane. Auxiliary methods of analyses are described (*249, 283*) designed to aid in resolving mixtures of isomeric compounds. Some factors affecting mass spectrometric analysis are considered by Nicholson (*227*). Herington (*138*) discusses the preparation and certification of standard hydrocarbon samples.

Grosse and coworkers apply the isotopic dilution method for the direct determination of oxygen in organic compounds (*116*), metals and metal oxides (*178*), and in fluorocarbon derivatives (*179*). Vacuum fusion is used by Hickam (*143*) to determine carbon, oxygen, and sulfur in copper. Kato (*172*) reports the analyses of gases contained in iron and steel, and Steyermark (*292*) describes a simple means of determining carbon in steel. Hess *et al.* (*141*) report on the measurement of trace quantities of uranium and lead in minerals and meteorites.

Blears (*27*) describes the application of the mass spectrometer to high vacuum problems. Hisatake and Matsuda (*148*) report on the mass spectrum of residual gases in the evacuated instrument, and Sites and Baldock (*276*) discuss studies of materials used in construction of high vacuum equipment.

Miller *et al.* (*211*) evaluate the carbon dioxide accumulation in anesthetized patients by means of a portable mass spectrometer analyzing the exhaled gases. Pratt *et al.* (*252*) describe the study of respiratory metabolism, and Brown *et al.* (*36*) report continuous recording of gaseous metabolism of cells, tissues, or complete organisms by means of the mass spectrometer.

PRECISE MASS MEASUREMENT

Many of the recent changes in atomic weights adopted by the commission on Atomic Weights of the International Union of Pure and Applied Chemistry are based at least in part on mass spectroscopic data. The accumulation of this data on substandards of atomic mass, the isotopes of hydrogen, helium and carbon, and other light atoms continues in many laboratories (*47, 82, 206, 231, 237, 238, 239*). The accuracy of mass spectrographic measurements is considered by Ewald (*81*). Bainbridge (*14*) compares values obtained from doublet and from disintegration measurements.

Collins, Nier, and Johnson (*48*), using a double-focusing instrument, redetermined doublets in the mass region of 40. They also report (*49*) the masses of 81 nuclides between mass numbers 31 and 70. Halsted (*122*), also using the University of Minnesota instrument, gives the atomic masses of 42 stable nuclides from palladium through zinc. Duckworth and coworkers (*109, 150, 151, 286*) report on a number of doublet and triplet measurements and associated atomic masses ranging from gallium to uranium. The stable isotopic masses of sodium and potassium are reported by Henglein (*132*).

Johnson (*169*) gives values for the masses of potassium-40 and for vanadium-50 (*168*). Recent work with the mass synchrometer on doublet measurements at masses 28 and 30 are reported by Smith and Damm (*281*). Goudsmit and coworkers (*131, 265*) describe further work with their time-of-flight instrument.

MEASUREMENT AND APPLICATION OF ISOTOPIC ABUNDANCE

Washburn, Berry, and Hall (*330, 331*) describe the techniques and conditions necessary for the direct isotopic analyses of water samples. Detectable differences in concentration of 0.0006 atom % deuterium in water containing about 0.015 atom % deuterium, 0.2 to 0.3 atom % deuterium in water containing 3 to 10 % deuterium, and 0.002 atom % protium in nearly pure deuterium oxide are reported. Epstein (*77*) presents further details on the performance of a mass spectrometer for the measurement of small differences in isotope abundance ratios. Reynolds and Ypsilantis (*264*) describe techniques in isotopic abundance measurements on elements of Group IV.

Baertschi and Schwander (*12*) present a method for measuring differences in oxygen-18 content of silicate rocks. A method for measuring the abundance of isotopes in the presence of residual peaks (*305*), a table for the calculation of nitrogen-15 concentration from mass spectral data (*1*), and a discussion of the decrease in N^{15}/N^{14} ratio measurement as a function of pump-out time for a Nier-type isotope ratio instrument (*111*) are also presented.

Several authors (*29, 40, 68, 115*) give details on the preparation of water samples for isotopic analysis by reduction to hydrogen over hot zinc or magnesium. Bigeleisen, Perlman, and Prosser (*26*) describe the conversion of various hydrogenic materials to hydrogen over hot uranium. Goodall and Alkire (*114*) report the method of equilibrating hydrogen with water using platinum oxide as a catalyst, and Dostrovsky and Klein (*66*) determine oxygen in water vapor by equilibration with carbon dioxide on platinum wire. Friedman and Irsa (*102*) determine low concentrations of deuterium in water by reaction with diethyl zinc to form deuteroethane. They point out, however, the necessity of complete reaction and the obvious interference of carbon-13.

Studies of natural variations in the relative abundances of isotopes of stable elements include: sulfur (*183, 300*), strontium (*6*), carbon (*333*), and silicon (*263*). Collins, Farquhar, and Russell (*43*) report wider variations in the abundances of the isotopes of common lead than previously observed by Nier. The isotopic constitution of palladium (*278*), ruthenium (*103*), silicon (*236*), and silicon, germanium, and hafnium (*262*) are recently reported. Palmer (*242*) discusses the accuracy and limitations of a Metropolitan-Vickers instrument for comparative isotopic abundance measurements of a number of elements.

Duckworth *et al.* (*71*) report the limits of abundance for hypothetical stable isotopes of hafnium and platinum. Measurement of carbon-13 in magnesium carbonate and in formic acid are reported by Hayakawa (*127*). The isotopic abundance of potassium-40 given by Reutersward (*259*) includes evaluation of possible mass discrimination by comparsion of the K^{39}/K^{41} ratio with that previously reported by Nier. Dansgaard (*56*) reports comparative measurements of United States, Swedish, and Danish standards for carbon isotopes.

Bentley (*23*) discusses the use of stable isotopes in biochemistry and the application of the mass spectrometer to biochemical problems. The isotopic composition of carbon is studied in some alkaline intrusions (*74*), minerals (*334*), Swedish graphites and limestones (*201*), and magmatic minerals (*309*). The relative abundances of the oxygen isotopes is determined in silicate rocks (*13*), carbonate rocks (*11*), and in various igneous, sedimentary, and metamorphic rocks (*275*).

The analysis of lead is reported for several minerals (*76*). Thode and coworkers discuss the distribution of sulfur-34 in nature and the origin of native sulfur deposits (*199*), and the isotopic constitution of igneous sulfur and the primordial abundance of the terrestrial sulfur isotopes (*198*). Craig (*53*) reports on the geochemistry of the stable carbon isotopes supporting previous work on carbon by Nier with greater detail.

The remarkable technique of establishing carbonate-water isotopic temperature scales and the measurements of paleo-temperatures and temperatures of the Upper Cretaceous of England, Denmark, and the southeastern United States are discussed by Urey and coworkers (*78, 313*). Geological age determinations in the Canadian shield (*44, 45*) and other uranium deposits (*293*) as well as estimates of the age of the earth's crust and maximum age of the elements (*46, 318*) based on lead isotopic abundance measurements are recently reported. Time scales are also based on isotopic abundance measurements of other elements. These include: helium and the age of meteorites (*244*), rubidium and strontium and the age of lepidolites (*58*) and other minerals (*306*), argon and the age of tektites (*295*), and sulfur (*301*).

NUCLEAR CHEMISTRY

Keim (*174*) describes the operation of mass spectrometers for enriching isotopes on a production scale, and gives a brief account of the associated chemical and analytical problems. Duckworth (*69, 70*) and Hogg and Duckworth (*153*) apply the mass spectrometer to the study of nuclear shell structure and give evidence for shell structure from atomic mass measurements. Inghram (*158*) outlines the use of the mass spectrometer as a tool for nuclear research and a number of authors report the application to nearly every phase of nuclear chemistry. These include: measurements of half-lives of radioactive isotopes (*161, 171, 327*), neutron capture cross-sections (*323*), decay energies (*152*), mass numbers of radioactive nuclides (*32*), fission yields (*335*), branching ratios (*270*), and double beta decay (*130*).

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Organic Polarography

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THE period since the last review has seen a great number of publications in the field of organic polarography. A stimulus in part for this increase was the first meeting of the Polarographic Congress in Prague in February 1951 on the occasion of the 60th birthday of Heyrovský, the founder of polarography. The numerous papers presented and submitted to this meeting consisted of new work and reviews. Among the latter were reviews on the polarography of organic compounds (*136*), polarography in organic analysis (*420*), biochemistry and medicine (*290*), in the paper and cellulose industry (*288*), in the study of kinetics in general (*317*), and on electrode processes in polarography (*32*), and specialized subjects which will be mentioned later.

Additional reviews in this field have appeared in other journals and have covered the historical developments of organic polarography (*391*), and applications to organic analysis (*331*), pharmaceutical analysis, control of medicine (*169*), organic compounds in general (*244*), organic compounds showing kinetic currents (*55*), oscilloscopic investigations (*144*, *206*), electrode processes in polarography (*362*), investigations of chemical kinetics (*316*), and the activities of the Polarographic Studies Center at Padova (*315*).

This period has again seen most of the studies carried out in mixtures of organic solvents and water. To aid solubility in such media the use of Aerosol MA and Aerosol AY (dihexyl and diamyl sodium sulfosuccinate) as solubilizers has proved effective for anthraquinone, lard peroxide, and *tert*-butyl hydroperoxide (*264*).

Work has continued to a small extent on the use of anhydrous solvents. Preliminary work on acetonitrile (*393*), alcohols, glycerol, pyridine, benzene and methanol, acetic anhydride and methanol (*133*, *134*, *387*), and 92% sulfuric acid has been reported (*379*, *380*). The actual use in the study of organic compounds of glycerol at elevated temperatures (*81*), acetone (*7*), dimethyl formamide (*96*), and 98.65% sulfuric acid has proved successful (*162*).

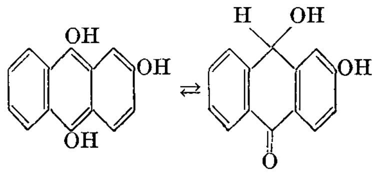
In the determination of the nature of electrode reactions new techniques for determining n have been devised and are dependent upon using micro scale polarographic cells and observing the drop in diffusion current with the time of electrolysis (*82*, *122*). A simplified method of measuring diffusion coefficients may prove of value to polarographers (*390*).

For the reproduction of polarographic data the importance of buffering action in the electrode processes (*78*, *199*, *200*) has been indicated and the effect of inadequate buffering capacity has been demonstrated with the reduction of azobenzene (*108*, *282*). Liquid junction potentials, which are also important in this respect, can be made more constant with a new type of agar salt bridge (*119*).

Work has continued with solid electrodes and has extended the polarographic method to the determination of phenols and alcohols (*120*, *142*, *208*).

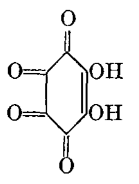
REVERSIBLE SYSTEMS

The polarographic method continues to be useful in determining the oxidation-reduction potentials of quinones. The values obtained for a series of anthraquinone sulfonic acids and hydroxyanthraquinones have been found to be in good agreement with the potentiometric data when available. Reversibility was indicated for all of these with the exception of 2-hydroxy- and 2,6-dihydroxyanthraquinone (*123*). Both of these in the reduced form undergo a tautomeric change with the formation of the corresponding anthranol and give an anodic wave which decreases with time (*124*).

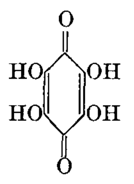


I II

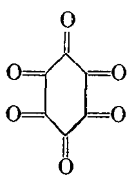
Similar agreement between polarographic and potentiometric data exists for rhodizonic acid (III), tetrahydroxyquinone (IV), and hexahydroxybenzene.



III



IV



V

Triquinoyl (V) is apparently not the quinone related to rhodizonic acid (III), as the latter (III) is not oxidized at the dropping mercury electrode. The small diffusion current obtained for the reduction wave of triquinoyl (V) indicated the possibility that it existed as a hydrate. No investigation was made, however, to see whether this was a kinetic current (*333*).

The polarographically determined reduction potentials for quinones agreed with the values calculated from the reduction curves of mixtures of quinones obtained using titanous chloride or platinum and hydrogen (*23*).

The method has been used to obtain normal potentials for 2-anilino-3-chloro-1,4-naphthoquinone and its *N*-ethyl derivative (*258*), 2-methyl-5-phenoxy-*p*-benzoquinone (*372*), and 2-(*o,m,p*-hydroxyphenoxy)-*p*-benzoquinones (*371*), and to study the reduction of 9,10-phenanthraquinone and acenaphthaquinone (*306*).

The reversibility of quinhydrone at the dropping mercury electrode has been used to demonstrate that carbonic anhydrase can increase the buffering action of carbon dioxide–bicarbonate buffers (*228*). In this quinone system the dyes eosin, erythrosin, and Rose Bengal have no effect on the reduction wave but will decrease the oxidation wave of hydroquinone (*192*).

The method has been used to determine the extent of hydrogen bonding in a series of hydroxyanthraquinones (*400*), to study the hydrolysis of 2-methyl-1,4-naphthoquinonimine (*186*), and to follow the oxidation of hydroquinone, pyrogallol, and ascorbic acid by hydrogen peroxide (*93*).

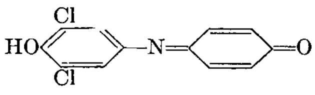
Quantitatively the reduction of quinones is successful in determining 1,4-naphthoquinone (*213*) in technical phthalic anhydride (*319*), vitamin K_3 (2-methyl-1,4-naphthoquinone) in foods (*406*) and prepared feeds (*242*), and vitamin K in pharmaceutical preparations (*374*).

Anthraquinone has been determined quantitatively in the presence of anthracene, phenanthrene, phthalic anhydride, and maleic anhydride in dimethylformamide as a solvent. The reduction process in this medium is interesting in that it goes through the semiquinone anion to the red hydroquinone dianion which can be actually seen at the mercury drop (*96*).

The reversibility of the catechol–*o*-benzoquinone system is questioned on the basis that wave analyses give values of 1.32, 1.39, and 1.15 instead of the theoretical value of 2. The E_0 for the system, however, agrees exceedingly well with the value obtained from static measurements for this compound (*398*).

The method has been used to follow the decomposition of adrenochrome with time and finds that the half-wave potential at pH 7.38 approximates that of codehydrogenase I (*412*).

In other reversible systems polarographic results for 2,6-dichlorophenolindophenol (VI) agree with those obtained by the classical method and indicate reversibility in a pH region between 4.1 and 11.7 (*354*). In strong alkaline solutions waves were obtained which changed on standing and pointed to decomposition of the compound (*355*).



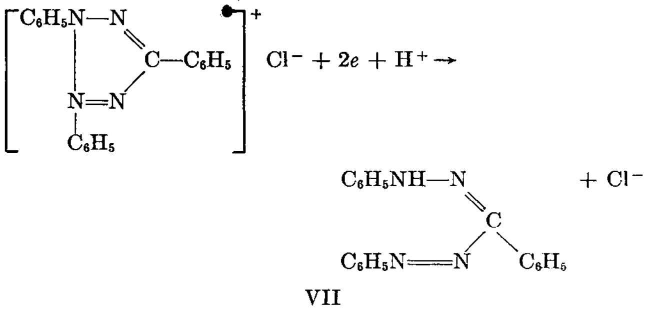
VI

Methylene blue, which gives an anomalous adsorption wave in addition to that expected on the basis of potentiometric data (*356*), behaves normally at the rotating platinum electrode (*357*). Equations derived for current-voltage curves at such an electrode, when applied to the data for methylene blue at pH 3.7, indicate that some hysteresis occurs on reversal of the potential (*368*).

The polarographic results have been found suitable for determining the stability, *K*, of the semiquinone of riboflavin and methylene blue and indicate that two electrons are involved in the reduction of natural (cozymaze, riboflavin) and artificial (methylene blue, oxazines) hydrogen carriers (*179*).

Methylene blue and similar dyes in small concentrations (*384*) have been found to form catalytic hydrogen waves.

The polarographic method has indicated that the photochemical decomposition of riboflavin produces a mixture of glycolic aldehyde and glyceraldehyde in addition to the lumichrome (*188*), has been used to determine riboflavin in tablets and ampoule solutions (*112*), and can give an approximate measure of the oxidative power of the biological oxidation-reduction indicators, 2,3,5-triphenyltetrazolium chloride (VII), 2,3-diphenyl-5-methyltetrazolium chloride, and 1-nitroanthraquinone, which are actually examples of irreversible systems (*94*).



VII

The various results reported for the azobenzene-hydrazobenzene system are conflicting and no definite statement can be made about the reversibility of this system at the dropping mercury electrode at the present time.

The reduction of *cis*- and *trans*-azobenzene is reported to be reversible in adequate citrate-phosphate buffers and irreversible in acetate buffers. The half-wave potentials varied 0.062 volt per pH unit and gave a slope corresponding to a two-electron change. No data were given on the oxidation of hydrazobenzene under these conditions (*52*). In 90% ethyl alcohol a similar behavior is observed at pH values less than 8.5. In more alkaline buffers the half-wave potentials differed and increased more rapidly with pH (*147*).

The only report on the oxidation of hydrazobenzene indicates that this process occurs at a more negative potential than that observed for the reduction of azobenzene under the same conditions. The adequacy of the buffers used in this study is questioned, since the slope analysis corresponded to one electron and the half-wave potential varied by 0.075 volt per pH unit (*107*). The sensitivity of this system to inadequate buffering is further demonstrated by the production of two waves in dilute acid solutions (*108, 282*).

In other work in this system the polarographic method has been used to follow the reaction between methyl orange and bovine serum albumin (*33*), to study the reduction of Neoprontosil (*373*) and Superchrome Garnet Y (*51*), and to determine the effect of various substituents on the reduction of azobenzene (*263, 378*) and 1-naphthylazobenzene (*378*).

IRREVERSIBLE SYSTEMS

ALCOHOLS AND PHENOLS

Methanol and ethanol give anodic waves at the rotating platinized platinum electrode which can be used to determine the latter in saliva (*208*). Phenols behave similarly at the graphite (*120*) and the microplatinum electrodes (*142*). The determination of phenol in waste liquor from coke plant ammonia in this manner gives a higher value than that obtained by the colorimetric and turbidimetric methods (*142*).

ALDEHYDES

The only basic work that has been done on these compounds has found that the behavior of acetaldehyde, propionaldehyde, isovalerylaldehyde, and several aromatic aldehydes at the sintered-glass filter electrode is similar to that at the dropping mercury electrode but less reproducible (*383*), and that the effect of temperature on the diffusion current of butyraldehyde and other compounds in the range 20° to 70° is about 2% per degree (*198*)

In other investigations the polarographic method has been used to determine formaldehyde in the presence of butyraldehyde (*28*), formaldehyde and acetaldehyde in various commercial products (*257*), unchanged formaldehyde in the phenol-formaldehyde condensation (*91*), acetaldehyde in the presence of propionaldehyde after fractionation by distribution between benzene and water (*74*), acetaldehyde in vinyl chloride (*67*) and in port wine (*5*), and acrolein in glycerol (*181*).

The polarographic method for aldehydes has been used to follow the reaction of formaldehyde with urea, *N*-methylurea, and *N*-ethylurea (*327*), and the formation of formaldehyde and acetaldehyde in the decomposition of dioxolane (*128*). The method shows that no formaldehyde is formed from methylene-bisurea on standing (*328*), that acetaldehyde and crotonaldehyde are formed in the cold flame oxidation products of 2-butene (*87*), and that the method is not satisfactory for obtaining hydration data for formaldehyde in high concentrations (*239*).

Indirectly the determination of formaldehyde and acetaldehyde may be used to determine 1,2-propylene glycol in ethylene glycol (*46*), and ethylene and propylene chlorohydrins (*47*). The chlorohydrins are hydrolyzed to glycols, which are then converted into formaldehyde and acetaldehyde by periodic acid.

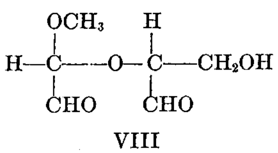
In the carbohydrate field a study of the kinetics of the ring-aldehyde transformation at the dropping mercury electrode has been made and equilibrium constants have been calculated for various sugars (*79, 80*).

The small reduction waves obtained for the sugars are responsible for the several indirect methods which have been devised for determining these compounds. Glucose can be determined in small amounts by titrating with potassium ferricyanide and following the change in concentration of the ferricyanide polarographically (*2*). Sugars in tannins are determined by treating with excess Fehling solution, filtering off the cuprous oxide, and polarographically determining the excess copper in the filtrate (*86*). Similarly, pentosans have been estimated in cellulose by converting them with hydrochloric acid to furfural and determining this compound polarographically (*90*).

In the only direct method mentioned, glucose and galactose give anodic waves at the rotating platinized platinum electrode which can be used for their estimation (*207*).

The polarographic method has been used to study the alkaline degradation of glucose. Possible products such as methylglyoxal, glyceraldehyde, acetoin, lactaldehyde, dihydroxyacetone, and diacetyl have been studied alone and together. The analysis of mixtures was aided by forming the quinoxalines of diacetyl and methylglyoxal and shifting the waves for these compounds (*335*). Of these possibilities glyceraldehyde on heating was found to give rise to three anodic waves similar in nature to those obtained for glucose in alkaline medium (*367*).

A study of the oxidation product (VIII) from methyl α-D-glucoside



$$\mathrm{H{-}\overset{OCH_3}{\underset{CHO}{C}}{-}O{-}\overset{H}{\underset{CHO}{C}}{-}CH_2OH}$$

VIII

has indicated in agreement with infrared data that the aldehyde groups are hydrated (*160*).

The polarographic estimation of surface active substances in sugars has been summarized in a recent review (*376*).

The polarographic method has been used to study the tautomeric change of crystalline streptomycin trihydrochloride to amorphous streptomycin (*143*), and gives good results quantitatively in 1*N* sodium hydroxide (*369*). That the aldehyde group is involved in the polarographic reduction has been confirmed by the formation of dihydrostreptomycin electrolytically at a mercury cathode (*236*).

Thirteen different unsaturated aldehydes in the terpene series have been studied polarographically and each has been found to give two waves (*309*). The wave for perilla aldoxime is suitable for polarographic determination (*222*).

In the aromatic series the polarographic method has been used to study the effect of ortho (*263*), para, and meta (*132*) substituents on the reduction of benzaldehyde. In the latter work (*132*), a plot of the half-wave potentials against the sigma constants of the substituents gave a straight line. The method has also proved successful in following the reaction of aromatic aldehydes with cyanide ion (*424*), and the disappearance of benzaldehyde in fermentation (*217*), and reports polarographic data for benzaldehyde, cinnamaldehyde (*70*), and phenylpropargylaldehyde (*262*).

A straight-line relationship is reported between the half-wave potentials of a series of unsaturated aldehydes and ketones and the difference between the energy levels of the product and reactant molecules at unit hydrogen ion activity. In this derivation the authors made an error in the quantum mechanical theoretical treatment of the product molecule and used two different approximations in their treatment of product and reactant molecules (*71*). The error has since been corrected by others, who derived a new expression and pointed out that the data were better fitted with an ellipse or parabola (*243*).

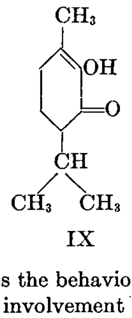
KETONES

Simple aliphatic ketones and other carbonyl compounds are found to be more easily reduced as oximes, *O*-methyl oximes (*382*), or condensation products with ammonia, primary amines (*419*), and glycine (*421*). The last three products are considered to be formed when the reduction of the ketone is carried out in the presence of the three compounds mentioned.

Diacetyl, the simplest α-diketone, is found to give one wave in a pH less than 7 and two waves in more alkaline media which correspond to a two-electron reduction. The product is considered to be 2-buten-2,3-diol, which then rearranges into acetoin (*255*). The latter is not reducible under the conditions used but can be determined indirectly by first oxidizing with ferric chloride to diacetyl (*256*).

The polarographic method has been used to follow the formation of diacetyl in butter (*89*).

A variety of straight-chain and cyclic α-diketones have been studied polarographically at a pH of 5.6 and found to undergo a one-electron reduction. The shift in half-wave potentials to more negative values, which was brought about by structural changes, was found to parallel the shift of absorption maxima to longer wave lengths observed with these compounds (*202*). Camphorquinone is reported by these investigators to give a one-electron reduction even at pH 12 in contrast to a two-electron change reported by others (*306*). The latter found that camphorquinone was a true α-diketone and not a quinone and that diosphenol (IX) behaved like an α,β-unsaturated ketone.



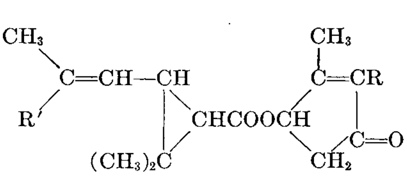
IX

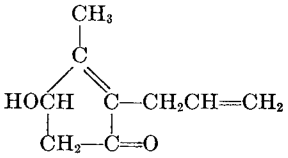
In the keto sugar series the behavior of the boric acid–fructose complex pointed to the involvement of the 2-keto group in the complex formation (*366*), and the polarographic behavior of *epi-meso*-inosose obtained by the nitric oxidation of *meso*-inositol has been reported (*69*).

A variety of α,β-unsaturated ketones have been studied polarographically, since this system is very common in natural products.

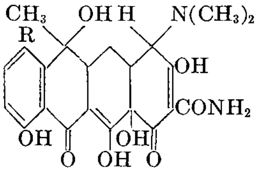
Polarographic data are reported for 5-membered (*308*) and 6-membered ring unsaturated terpene ketones (*307*), for α-ionone, β-ionone, 4-(2′, 6′, 6′-trimethylcyclohexen-1-yl)-2-methylbuten-2-al (*54*), and hepta-2,4-dien-6-one (*70*).

Natural and synthetic pyrethrins (X) which have this unsaturated system give similar curves, which are suitable for quantitative estimation (*409*). The geometrical isomers of allethrin (X, R = allyl) give the same wave at a pH of 2.97. This wave can be used for quantitative work only in the absence of allethrolone (XI) which is reduced at the same point (*237*). The latter (XI) can also be determined polarographically in the presence of various related industrial products (*238*).


X

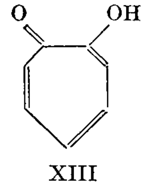

XI

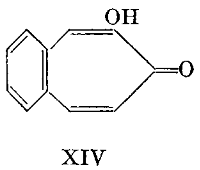
The antibiotics Aureomycin (XII, R = Cl) (*95*) and terramycin (XII, R = H) give waves which are proportional to concentration (*194*) and which have been used to study the alkaline inactivation of Aureomycin (*92*).


XII

Colchicine, which gives two reduction waves below pH 8 (*299*), shows an identical polarographic behavior to that of a sample containing radioactive carbon (*388*). The reduction has been used to determine the amount of colchicine in the plant and seeds of the meadow saffron (*36*) and to follow the content of colchicine in the development of the flower (*35*).

Tropolone (XIII), β-methyltropolone, and β,γ-benzotropolone (XIV) behave polarographically like colchicine.


XIII


XIV

The last compound (XIV) shows the most positive potential (*231*). The results for tropolone differ from those reported by James and Speakman (*163*). The discrepancies are ascribed to the use of inadequate and complex-forming borate buffers by the latter two investigators.

In the acetophenone series polarographic studies have been made on the effect of groups in the ortho position, in the methyl group (*263*), and in the para and meta positions on the ease of reduction (*38*, *132*).

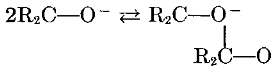
The method can be used to determine compounds which are easily converted by acetylation into acetophenones (*413*).

Studies on benzophenone (*118*) and related compounds have given a better insight into the mechanism of their polarographic reduction in acid and alkaline media. Fluorenone has been found to have a great tendency to form double waves followed by benzanthrone, benzophenone, and α-benzoylnaphthalene (*77*). This behavior parallels the effect of the groups in promoting free radical stability; 9-fluoryl is least effective, followed by benzanthryl, phenyl, and 2-naphthyl.

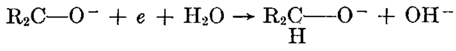
A similar relationship holds for xanthone and p-chlorobenzophenone. Xanthone gives only one wave in all the buffers studied. The xanthyl group has a greater stabilizing effect on free radicals than two phenyl groups (*76*).

These studies are in agreement with the previously proposed mechanism by Ashworth for the reduction of the ketones at high pH values.

$$R_2C{=}O + e \rightleftarrows R_2C{-}O^- \qquad (1)$$



$$2R_2C{-}O^- \rightleftarrows \begin{matrix} R_2C{-}O^- \\ | \\ R_2C{-}O^- \end{matrix} \qquad (2)$$



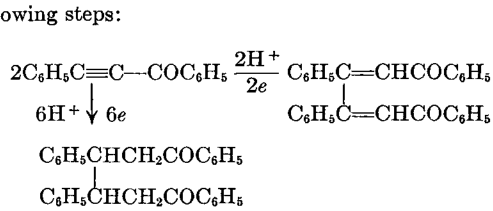
$$R_2C{-}O^- + e + H_2O \rightarrow \underset{H}{R_2C}{-}O^- + OH^- \qquad (3)$$

The position of the equilibrium in Equation 2 will determine the number of waves observed in alkaline medium and is affected by the groups present and cations in solution. The behavior is analogous to that observed for the reduction of complex metal ions.

Other studies in this series have been concerned with the effect of groups in the benzene ring on the ease of reduction of the carbonyl grouping (*25*, *34*, *263*).

The polarographic behavior of benzoin and benzil has been reinvestigated (*27*). The reduction, which has been considered to proceed in a 1,4-manner and to give an enediol, has been rather unusual in that no wave has been found for benzoin which would be formed by the isomerization of the intermediate. Recent studies, however, report the existence of such a wave (*117*) which is, however, lower than what would be expected for benzoin and suggests that the rearrangement of the enediol to benzoin is slow at the electrode (*263*). Such an explanation is further borne out by the reduction of the mesityl analog for which the enediol is stable; the second wave is not formed.

The reduction of α,β-acetylenic ketones has been compared with that of their ethylenic analogs and can be best explained by the following steps:



$$2C_6H_5C{\equiv}C{-}COC_6H_5 \xrightarrow[2e]{2H^+} \begin{matrix} C_6H_5C{=}CHCOC_6H_5 \\ | \\ C_6H_5C{=}CHCOC_6H_5 \end{matrix}$$

$$\downarrow 6H^+\ 6e$$

$$\begin{matrix} C_6H_5CHCH_2COC_6H_5 \\ | \\ C_6H_5CHCH_2COC_6H_5 \end{matrix}$$

The behavior of bisphenyl ethynyl ketone was found to be more complicated (*262*).

Extensive work on the reduction of oximes has been carried out. Benzophenone oxime is more easily reduced than the ketone in acid medium and less readily in basic medium. From a pH of 7.3 and on a drop in the diffusion current occurs followed by a rise at more negative potentials. The first wave is kinetic in nature and points to the involvement of an equilibrium reaction at the electrode. The reduction in most cases involves four electrons and gives the amine. The drop in current is not observed with all the examples studied (*332*).

Data are also reported by others on benzophenone oxime (*45*), acetophenone oxime (*44*), substituted acetophenone oximes (*263*), α-benzoin oxime (*42*), β-isatin oxime (*40*), salicylaldoxime (*41*), and pinocarvonoxime (*306*).

ACIDS AND THEIR DERIVATIVES

The behavior of a series of simple acids has been studied at the dropping mercury electrode (*24*) and results found to point to a slow dissociation of the acids at the electrode (*210*).

The method has been used to determine phthalic acid in the presence of benzoic acid (*324*) and phthalate esters in ethylcellulose and cellulose acetate (*399*), and to study the reduction of acid halides in acetone (*7*).

No correlation has been obtained between the effect of various phenoxyacetic acids and benzoic acids on the oxygen maxima and their physiological activity as plant growth materials (*246*).

In the hydroxy acid series tartaric acid can be determined polarographically as the antimonyl complex (*216*), and salicylic acid is reported to give a reduction wave in a tetrabutylammonium hydroxide solution (*129*).

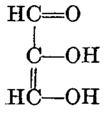
Pyruvic acid, like other carbonyl compounds, is reduced more easily in the presence of glycine, alanine, ethanolamine (*416*), ammonia (*101, 415*), histidine, and histamine (*414*).

The polarographic results for this acid have been extensively used to check theoretically derived equations for the kinetic current observed (*79*) and for the change in half-wave potential with pH (*359, 361*). In a similar fashion the results for benzoylformic acid have been used to check calculations based on the equations of Koutecky and Brdicka (*135*).

The polarographic method has been used in the unsaturated acid series to determine crotonic acid (*125*), methacrylonitrile (*330*), acrylonitrile (*19*), anhydrides of α,β-unsaturated acids (*271*), and mixtures of maleic and furmaric acids and their ethyl esters (*98*).

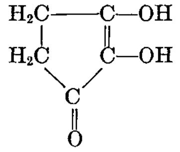
Polarographic data are present for fumaric acid in the presence of phosphate buffers (*254*) and in the pH region 4.78 to 8.2 (*253*), for styrylacetic acid (*240*), acetylene dicarboxylic acid, phenylpropiolic acid (*262*), and both *cis, cis*- and *trans, trans*-muconic acids (*103*). The reduction of the last acid was used to prove that *trans, trans*-muconic acid was a product of the oxidation of benzene by a soil microorganism (*184, 185*).

The oxidation at the dropping mercury electrode observed with ascorbic acid occurs only with a limited number of compounds such as D-araboascorbic acid, glycoreductone (XV), reductinic acid (XVI), and dihydroxymuconic acid (XVII) (*250*).

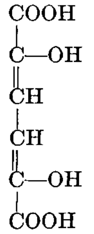


$$\mathrm{HC{=}O{-}C(OH){=}CH{-}OH}$$

XV



XVI



$$\mathrm{COOH{-}C(OH){=}CH{-}CH{=}C(OH){-}COOH}$$

XVII

The reduction of dehydroascorbic acid, the oxidation product of ascorbic acid, occurs only in the presence of ammonia (*416*) or at a high concentration of the acid because of its hydrated structure (*241*).

The method is suitable for determining combined ascorbic acid (*423*) and ascorbic acid in the presence of glutathione but not of reductone (*126*). The use of a platinum electrode in this analysis determines not only ascorbic acid but also a substance oxidizable at more positive potentials (*325*).

In other work a relationship between the half-wave potentials obtained for the reduction of the α,β-unsaturated ketone system of β-aroylacrylic acid derivatives and the antibacterial activity of the compounds is reported (*392*) and nitrate esters are found to give a reduction wave involving two electrons (*175*).

$$\mathrm{RONO_2} + 2e \rightarrow \mathrm{RO^-} + \mathrm{NO_2^-}$$
$$\mathrm{RO^-} + \mathrm{H_2O} \rightleftarrows \mathrm{ROH} + \mathrm{OH^-}$$

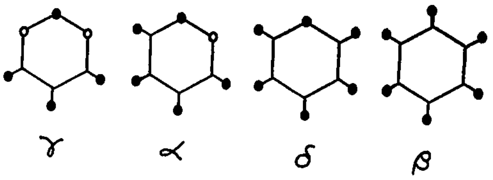
The wave for this reduction is not as well defined in anhydrous solvents (*267*).

ORGANIC HALOGEN COMPOUNDS

Reinvestigation of the unusual polarographic behavior of allyl iodide indicates that the allyl iodide reacted with mercury to form allylmercuric iodide and that the latter was responsible for the behavior reported (*63*).

The method has been used to follow the hydrolysis of benzyl chloride (*298*) and various para-substituted benzyl chlorides (*64, 297*).

An extensive review of the polarographic behavior of hexachlorocyclohexanes and related compounds in terms of their structures has been presented (*230*). It is interesting to note that the γ- isomer, which has three polar halogens, is more easily reduced than the α- isomer, which has two, and that in turn more easily than the δ- isomer, which has one. β-Benzene hexachloride, in which all the chlorines are equatorial, gives no reduction wave.



The term "polar" used with these compounds refers to the chlorines which are perpendicular to the plane of the equatorial chlorines and has nothing to do with electrical charges.

The polarographic method for determining the γ-isomer can be carried out using alcohol as the solvent and sodium chloride as the electrolyte (*196, 197*), or at a pH of 11.5 if heptachloro compounds are present. The latter compounds are destroyed under these conditions and do not interfere in the analysis (*225*). The analysis gives values which are in good agreement with the biological test (*138*) and actually requires only three points to establish the curve (*411*).

The reduction of γ-hexachlorocyclohexane at constant potential, which requires six electrons and forms benzene (*114*), has been made the basis of an electrolytic method for determining the γ-isomer (*305, 310*).

The polarographic method for hexachlorocyclohexane has been reviewed (*174*), and has been used to determine the γ-isomer in ointments and lotions (*111*) and to follow the alkaline elimination of hydrogen chloride from the δ-isomer (*164*). By means of this technique it has also been possible to follow the electroreduction of DDT to DDD (*115*) and to study the reduction of halogenated terpenes (*306*).

In the α-halogenated carbonyl compound series the effectiveness of various groups on the reduction of halogens has been pointed out (*182*), and the effect of carbon chain length (*276*) and branching on the reduction of α-halogen acids have been described (*286*). Studies have been also reported on the various chloroacetic acids and their ethyl esters (*99*), and a way indicated for predicting the half-wave potentials of chloroacetic and dichloroacetic acids (*277*).

Polarographic data are presented for α-chloromethylethyl ketones (*26*) and α-chlorovinylacetic acid (*183*).

In a review on the polarography of iodo compounds the behavior of the iodine contrast agents, Diodone, Iodoxyl, and Pheniodol, is described (*245*).

The method in this series has been used to study the reduction of various iodinated benzoic acids, anilines, phenols, nitrobenzenes (*121*), and phthalic acids (*97*), to assay the amount of I^{131}-labeled thyroxine prepared from diiodothyronine (*57*), to determine the amount of thyroxine in tablets (*3*), and to follow the iodination of α-phenyl-β-4-hydroxyphenylpropionic acid to pheniodol (*113*).

Halogens in organic compounds have also been determined by destroying the organic matter with sodium and potassium and determining the halide formed polarographically (*293*).

Phenyliodonium salts in 50% ethyl alcohol give four reduction waves, for which the following steps can be written (*60*):

1st wave	$(C_6H_5)_2I^+ + I^- \xrightarrow{+e} C_6H_5I + C_6H_5\cdot + I^-$ $C_6H_5\cdot + Hg \rightarrow (C_6H_5)Hg\cdot$ $2C_6H_5Hg\cdot \rightarrow (C_6H_5)_2Hg + Hg$
2nd wave	kinetic, process unknown
3rd wave	$(C_6H_5)_2Hg + 4e + 2H^+ \rightarrow 2C_6H_6 + Hg$
4th wave	$C_6H_5I + 2e + H^+ \rightarrow C_6H_6 + I^-$

In ethylene chloride as a solvent only the first wave is observed (*61*).

The iodosobenzene-iodoxybenzene system has been found to be irreversible at the dropping mercury electrode. Iodosobenzene gives an anodic wave which occurs at a different point from the reduction wave for iodoxybenzene (*58*). The reduction of the two compounds is reported to occur at the same point and to give iodobenzene. There is some disagreement on the effect of pH on the first reduction wave (*110*).

Chlorosilanes are not reducible polarographically but form in pyridine the reducible pyridinium ion which can be used for their estimation (*1*).

NITRO COMPOUNDS

The reduction of aliphatic nitro compounds at the dropping mercury electrode has been limited to a study of their behavior in anhydrous solvents in which the waves were found to be not as well defined as in water (*81, 267*).

The polarographic behavior of aromatic nitro compounds has been investigated in a variety of solvents. Results are reported for a number of these in 98.65% sulfuric acid (*162*) and in glacial acetic acid (*16*). The spread in half-wave potentials in the latter is much greater than that in the sulfuric acid.

Considerable work has been done on the effect of surface active substances on the reduction wave of various aromatic nitro compounds. Gelatin and pyridine have been found oscillographically to make the reduction go stepwise (*146*). A similar effect has been found polarographically for gelatin (*360*), agar, tylose of varying degrees of polymerization (*151, 153, 156*), and camphor (*154*). Various explanations have been offered for this phenomenon (*336*).

The polarographic method has been used to study the effect of steric hindrance on the reduction of nitro groups (*263*), to prove the presence of chelation in *o*-nitroaniline (*284*), *o*-nitroacetanilide, and *o*-*N*-nitrophenyl-*N'*-phenylacetamidine (*285*), to show that a relationship similar to that of Hammett's existed between the reduction potentials of substituted nitrobenzenes and the corresponding dissociation constants of the substituted benzoic acids (*189*), and to compare the effects of groups upon the mechanism of reduction of a series of dinitrobenzenes, anilines, phenols, toluenes, and chlorobenzenes (*155*). *m*-Dinitrobenzene, which gives two waves under these conditions, was found to give three waves at a mercury plated platinum electrode in quiet and stirred solutions (*212*).

Polarographic data are reported for 4-nitro-4'-bromo-, 4-nitro-4'-chloro-, and 4-nitro-4'-hydroxybiphenyl ethers (*215*), 2,2'-dinitrobiphenyl, 2,2-dinitrosobiphenyl, benzo(*c*)cinnoline-5-oxide, and benzo(*c*)cinnoline (*278*). Quantitatively the method has been used to determine mononitronaphthalenes and dinitronaphthalenes in the presence of each other (*173*), nitrobenzene in blood (*116*), and hydroxynitrophenylarsonic acid (*283*).

The reduction of sodium dipicrylaminate serves as the basis for the amperometric titration of potassium (*410*) and is carried out best at a pH of 11.5 to 12 (*223, 287*). Picric acid has been used in a similar fashion to determine scopolamine (*395*). The latter may also be nitrated and determined polarographically as the 2,4-dinitro derivative (*396*).

Indirectly the polarographic method has been used to determine phenol in water and urine (*280*) and benzene in illuminating gas by nitrating each to the polarographically reducible nitro compounds (*261*). In a similar fashion cholesterol can be determined by forming the 3,5-dinitrobenzoate and studying this compound (*234*).

The polarography of aliphatic and aromatic nitro compounds has been reviewed (*313*), and the values for nitrobenzene used to check the validity of a derived expression for polarographic curves (*342*).

NITROSO COMPOUNDS

The reversibility of the aromatic nitroso-hydroxylamine system at the dropping mercury electrode has been verified in the benzene and naphthalene series (*152*).

DIAZONIUM SALTS

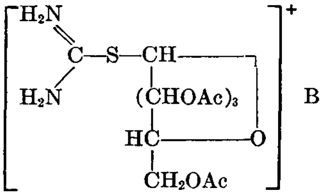
The mechanism of reduction of diazonium salts has been rechecked on a large scale and found to involve two electrons at a potential corresponding to that of the second wave (*8*).

The reduction of these salts has been used as a basis for the amperometric titration of cephaeline, emetine (*166*), and various quinoline compounds (*167*), and to demonstrate the ability of a cathode-ray polarograph with a permanent recorder to follow a coupling reaction which is complete in 120 seconds (*329*).

The method can be used to determine 5-aminosalicylic acid in the presence of *p*-aminosalicylic acid, and *m*-aminophenol in the presence of *p*-aminosalicylic acid by diazotizing and examining the products polarographically (*170*).

AMINES, AMINO ACIDS, AND DERIVATIVES

A polarographic study of Crystal violet, Brillant green, Malachite green, and Auramine gave indications for the formation of a stable semiquinone (*177*). A similar study of *S*-(polyacetyl-β-D-glycopyranosyl)-thiuronium halides of sugars (*30*) indicated that they are all reduced at the same point. In other work amines such as the various antihistamines gave curves that were not reproducible (*18*), and *O*-methylhydroxylamine gave a reduction wave only in acid media (*381*).



Most of the polarographic determinations of amino acids are done indirectly. Tyrosine (*226*) and tryptophan are determined by nitrating beforehand to reducible derivatives (*17, 224*). Ethylenediaminenitrilotriacetic acid and ethylenediaminetetraacetic acid are determined by conversion to the reducible copper complex (*75*). *p*-Aminosalicylic acid is determined with bromine by following the concentration of the latter with a rotating platinum electrode (*204*).

UNSATURATED HYDROCARBONS

Comparisons between the half-wave potentials of aromatic hydrocarbons and the coefficient of the molecular orbital resonance integral in the expression for the energy of the lowest unoccupied orbital of these compounds has been extended to polynuclear aromatic hydrocarbons (*15, 265, 266*). A similar straight-line relationship is obtained if the zero-order molecular orbital method of Hückel is used (*150*).

Vinylcycloöctatetraene is found to give a reduction wave approximately at the same point as cycloöctatetraene (*320*). The latter when reduced electrolytically on a large scale gives a mixture of 1,3,6-cycloöctatriene and 1,3,5-cycloöctatriene (*72*).

Polarographic data are given for azulene, various alkylated azulenes (*56*), and indene (*260*).

Indirectly unsaturated hydrocarbons can be determined by titration with bromine and following the change in the reduction wave of bromine with a rotating platinum electrode (*21*).

PEROXIDES AND HYDROPEROXIDES

Hydroperoxides, benzoyl peroxide, and succinic acid peroxide are reducible polarographically in a mixture of benzene and methanol containing lithium chloride; di-*tert*-butyl peroxide and compounds with the oxirane ring are not affected (*405*).

The method has been used to follow the oxidation of methyl oleate (*247, 343*), to prove the presence of alkyl hydroperoxides in products from the cold flame oxidation of butane (*88*) and the mercury-sensitized photochemical oxidation of propane (*109*), to study the nature of the peroxide formed in autoxidized lard, methyl oleate, and related compounds (*233*), to show that terpene hydrocarbons easily pick up air and form peroxides (*306*), and to determine ascaridole in oil of chenopodium (*11*) and in oil of Boldo (*20*).

Ethyl hydroperoxide may be determined at a vibrating platinum microelectrode (*273*).

The work on the polarography of ether peroxides has been summarized (*270*).

SULFUR COMPOUNDS

Sulfonic acids derived from aliphatic dienes (*364*), pyrrols (*365*), and indoles (*363*), when present as barium salts in a solution containing 0.5N potassium chloride and 0.003N hydrochloric acid, are reported to give anodic waves which are dependent upon the structure of the compound.

Methanesulfonyl chloride and various benzenesulfonyl chlorides have been found to give reduction waves corresponding to a two-electron change (*209*).

$$RSO_2Cl + 2e \rightarrow RSO_2^- + Cl^-$$

Alkyl and aryl sulfonates behave similarly and, at least the former, by analogy to the alkyl halides, must give the hydrocarbon and the sulfonate ion (*211*).

$$RSO_3R + 2e + H^+ \rightarrow RSO_3^- + RH$$

Aromatic sulfones and sulfoxides are likewise reported to give reduction waves of four and two electrons, respectively (*211*). An alkylaryl sulfone such as 2,3-dihydrobenzothiophene-1-dioxide is reported, however, to give no reduction (*326*). A double bond if conjugated with the sulfone group as in benzothiophene-1-dioxide or methylvinyl sulfone, gives a reduction wave. This reduction, which can go by 1,4- addition only if sulfur expands its shell to ten electrons, resembles the reduction of unsaturated hydrocarbons rather than that of methylvinyl ketone, in that one wave is obtained which is independent of pH (*168*). Such a behavior suggests a different reduction mechanism from that of unsaturated ketones. The last investigators in their discussion misinterpreted previous work that had been published on unsaturated ketones (*168*).

Sulfonium salts give a reduction wave which corresponds to a two-electron change (*59*). The actual mechanism is not known, but the large scale reduction of triphenylsulfonium halides gives diphenyl sulfide and products resulting from a phenyl free radical (*29*).

The reduction of *p*-dimethylaminophenylthiocyanide has been studied on a large scale and found to form *p*-dimethylaminothiophenol and hydrogen cyanide (*311*).

Carbon disulfide can be determined polarographically by making use of its reduction wave (*144, 190*) or by adding it to an ethyl alcohol solution of diethylamine and using the anodic wave of the diethyldithiocarbamate formed (*426*).

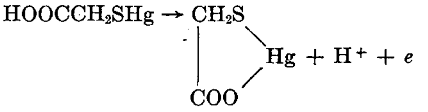
Reduction curves are reported for alkyl disulfides, *tert*-butyl trisulfide, and polysulfide (*130*), and dimethylcarbamyldimethylthiocarbamyl disulfide [$(CH_3)_2NCOSSCSN(CH_3)_2$] (*127*).

The polarographic behavior of α-lipoic acid pointed to a cyclic disulfide structure (*269*) but was not adequate to judge the ring size (*268*).

Anodic waves involving the formation of mercurous salts are given by diethyldithiocarbamic acid (*39, 295*), thiourea (*300*), thioglycollic acid (*203, 205*), and glutathione (*338, 347, 351*). When a carboxyl group is present with the thiol grouping as in thioglycollic acid and glutathione, a second anodic wave is obtained which is believed to involve further oxidation of the mercurous salt.

1st wave $HOOCCH_2SH + Hg \rightarrow HOOCCH_2SHg + H^+ + e$

2nd wave



$$HOOCCH_2SHg \rightarrow \begin{array}{l} CH_2S \\ | \quad \diagdown \\ | \qquad Hg + H^+ + e \\ | \quad \diagup \\ COO \end{array}$$

The polarographic reduction of dithiodiglycollic acid and of oxidized glutathione proceeds normally and gives thioglycollic acid and glutathione, respectively (*203, 350*).

An equation has been derived for the polarographic behavior of the thiol-disulfide system (*349*).

The polarographic method can be used to determine cystine in the presence of glutathione (*337*) and SH compounds in fruits and can distinguish between these compounds and ascorbic acid (*417*).

The diminution produced in the first reduction wave of sodium *p*-chloromercuribenzoate by compounds containing SH groups can be used as a quantitative measure for the thiol compounds (*139*), since the phenylmercuric mercaptides formed are reduced at more negative potentials. The product from phenacetyl-L-cysteinyl-D-valine and phenylmercuric hydroxide behaves differently from those of other peptides under ordinary conditions and shows a normal behavior only in the presence of urea. It has been suggested that S–H–N bonding stabilizes the SH group and gives the abnormal behavior (*13*).

The Brdicka test, in which a catalytic wave is produced by a substance in a solution of cobalt chloride, ammonium chloride, and ammonia, is given by cystine (*131*), and can be used to determine the cystine content in protein hydrolyzates (*406*). The test has been used on α-casein, β-casein, serum albumin, egg albumin (*140*), egg white fractions, alkali, and urea denatured ovalbumin (*141*), sera from cancerous animals (*229*), milk (*339*), proteins fractionated by microelectrophoresis (*157*), serum from experimental cancer (*73*), denatured blood serum at various temperatures (*302*), and various proteins (*219*). The test has been used as evidence for thiol groups in enzymes (*323*), finds no thiol groups liberated in the addition of thrombin to fibrinogen (*220*), and has been applied to the study of various diseases (*303, 377*) and the indirect determination of pepsin (*159*). The possibility of a relationship between this test and carbohydrate metabolism has been suggested (*158*) and the use of the test in detecting cancer in clinical work has been reviewed (*274*).

The effect of macromolecular substances upon the anodic curve obtained with potassium iodide and sulfuric acid has been found to be characteristic for a number of these (*172*).

ORGANOMETALLIC COMPOUNDS

The mechanism previously proposed for phenylmercuric compounds was confirmed polarographically and oscillographically (*385*) and the nature of the adsorption curve demonstrated (*14*).

The polarographic method has been used to determine phenylmercuric nitrate (*408*), and to follow the decomposition of olefin-mercuric chloride addition compounds (*281*) and the reaction of glutathione and BAL with various aromatic mercuric compounds (*12*).

The polarographic behavior of alkyl lead, mercury, tin, and thallium halide compounds is interpreted and discussed (*62*).

Vitamin B_{12} has been investigated polarographically by several groups (*84, 85, 304*) and the results point to a reduction from cobalt(III) to cobalt(II), since the vitamin when treated with chromium chloride will give a product which shows an anodic wave similar to that shown by divalent cobalt (*31*). The product obtained by catalytic hydrogenation shows an entirely different polarographic behavior.

The polarographic method for this vitamin is reported inferior to the absorption spectroscopy method for quantitative determination (*83*).

Vitamin B_{12} may be also determined by ashing the sample and determining the cobalt polarographically (*100*).

The interesting compounds formed from cyclopentadiene and various metals such as iron [ferrocene, $(C_5H_5)_2Fe$] (*403*), ruthenium (*401*), and nickel (*402*) give anodic waves at the dropping mercury electrode. Compounds such as cobalticinium perchlorate, $(C_5H_5)_2Co^+ \ ClO_4^-$, (*401*), biscyclopentadienyltitanium dibromide (*402*), and rhodicinium perchlorate gave reduction waves. The iridicinium (*68*) and zirconium compounds showed no reduction (*402*).

OXYGEN HETEROCYCLIC COMPOUNDS

Cardiac glucosides such as strophanthin, which have an aldehyde group on C_{10}, give a reduction wave in an alkaline glycine buffer which is for the condensation product formed. This wave can be used for quantitative purposes and is characteristic only of compounds with this structure (*425*).

Previous polarographic work on heart poisons has been summarized (*289*).

The method has been applied to the determination of heart glucosides separately or in mixtures (*322*), digitoxin and gitoxin (*148*), and the sapogenin, 9,11-dehydromanogenin (*272*).

The polarographic reduction of coumarin has been verified (*48, 248*) and extended to a variety of substituted coumarins (*106, 227, 249*). The rapid hydrolysis observed for coumarin in alkaline solution has been followed oscillographically (*102*).

Anthocyanins and anthocyanidins are reducible polarographically and can be determined by this method in plant materials (*418*).

The polarographic method has been used to determine khellin in serum (*37*) and tocopherols in vegetable oils by first oxidizing these to the easily reducible tocoquinones with ceric nitrate (*187*).

Polarographic data are reported for coumarone (*260*).

NITROGEN HETEROCYCLIC COMPOUNDS

Polarographic studies are reported for 1-butyl-3-pyrrolidone in acid solution (*201*) and pyridine (*178*), and picolines and 2,6-lutidine in unbuffered media (*259*). Impurities in pyridine which cause polarographic waves can be removed by forming and distilling the hydrochloride and then regenerating the pyridine (*386*).

Acid hydrazides in the pyridine series, which are important in the treatment of tuberculosis, have been intensely studied polarographically. The most important member, isonicotinyhydrazide, gives a reduction wave and an anodic wave. The reduction wave corresponds to a four-electron change, but the actual reduction mechanism is not known. The anodic wave occurs at the same point as hydrazine and can in combination with the cathodic wave be used for determining the amount of hydrazine present. Buffers with a pH of 9 (*6*), 7 (*214*), 6.52 (*352*), and 1.5 (*232*) have been found suitable for the quantitative estimation. The precision for the determination is ± 1% (*312*).

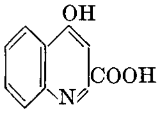
The method has been used to study the relationship between the half-wave potential and the antitubercular behavior for nicotinamide and a variety of heterocyclic compounds (*275*) and to help in the identification of nicotinamide isolated from squamous-cell carcinomas (*49, 50*).

The polarographic behavior of dihydroxyindole (*191*) and *N*-alkylisatins is reported. The behavior of the latter is found to be analogous to that of isatin itself (*341*).

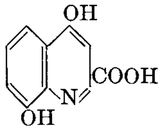
Quinoline like acridine was found to give a polarographic wave free of distortions in 50% ethyl alcohol (*178*).

Polarographic studies of analytically important derivatives of quinoline have been summarized (*334*), extended to various methyl 8-quinolinols (*104, 105*), the product from 8-quinolinol and hydroxylamine ("indo-oxine") (*251*), 8-quinolinol-5-sulfonic acid and the corresponding quinaldine derivative (*252*), and repeated for quinaldic acid (*394*).

The polarographic method has been used to show that quinoline and pyridine oxides are more stable to reduction than amine oxides (*235*), to examine the behavior of nicotinic acid and tryptophan metabolities such as kynurenic (XVIII)



XVIII



XIX

and xanthurenic acids (XIX) (*318*), and to prove that the reduction of quinine involves the quinoline ring (*10*).

The determination of morphine polarographically, which is dependent on preforming the nitroso derivative, can be carried out in alkaline solution (*218*), and has been used to determine this compound in mixtures of opium alkaloid (*397*) and to follow its content in the growth of the poppy (*9*).

Compounds related to morphine such as codeinone, metathebainone, etc., because of their α,β-unsaturated ketone structure are directly reducible at the dropping mercury electrode. The dihydro compound also gives a wave which is ascribed to the splitting of the furan ring. The possibility that this wave represents a reduction of the ketone group has not been excluded (*291, 292*).

N-Allylmorphine hydrochloride gives a polarographic wave which is considered to involve the reduction of the allyl double bond. Since this group has been shown in simpler derivatives to be resistant to polarographic reduction, the possibility of a cleavage of the allyl group from the nitrogen must be considered as an explanation for the reduction (*314*).

In the acridine series the polarographic behavior of a series of aminoacridines and their physiological activity have been compared (*176*) and the order of their reduction found to correlate with the change of unsaturated energy involved in passing from the ionized aminoacridine to the ionized acridyl radical (*161*).

The important acridines, trypaflavine, atebrin, proflavine, and rivanol, have been determined polarographically (*22*).

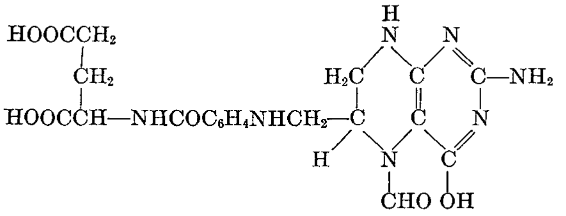
Polarographic studies are reported for arecaidine benzylidene hydrazide (*294*), cephaeline (*165*), erythrophleine, erythrophlenic acid (*358*), jervine, veratramine, veratrosine (*389*), lobeline (*370*), nornicotine (*404*), 1,10-phenanthroline (*195*), and the chlorophyllins (*407*).

Reduction waves are also observed for heterocyclic compounds containing two and three nitrogen atoms in the ring. Examples and related compounds that have been studied are parabanic acid, oxaluric acid, allantoxamic acid (*149*), cyanuric acid, rubeanic acid, cyamelide, (*340*), various pyrimidines (*53*), and phenazine (*178*).

Barbituric acid (*193*) and veronal (*422*) give two anodic waves which represent the formation of a mercuric complex. The first of these is an adsorption wave and can be used for determining concentrations up to $10^{-3}M$ if a streaming mercury electrode is used.

Barbituric acid derivatives may also be determined polarographically by titrating with mercuric salts and following the change of the latter polarographically (*171*).

Polarography has played a very important part in the structural evaluation of the growth factor leucovorin.



This compound is not reducible as such at the dropping mercury electrode but when treated with hydrochloric acid and then adjusted to pH 9, is easily oxidized by air to an unreduced pteridine and a compound reducible at about the same potential as dihydropteroylglutamic acid. The anodic and cathodic waves obtained can be used to determine leucovorin quantitatively and when compared with the results for other pteridines are useful in the evaluation of structure (*4*).

Synthetic leucovorin (*279*), *dl*-leucovorin (*66*), and the 1-methyl analog of leucovorin showed a similar polarographic behavior (*65*).

Folic acid can be determined polarographically in the presence of thiamine, riboflavin, and niacin (*375*).

Benzylpenicillin at 0° C. and a pH of 2 using oscillographic (*145*) and polarographic analysis (*137*) gives no reduction waves. After a few minutes two waves appear for penicillenic acid, which increase and then decrease when this acid decomposes.

Saccharin gives the same polarographic behavior as its sodium salt (*353*) and can be determined in the presence of invert sugar (*222*) and coloring matter (*180*).

Anodic waves with the formation of mercurous complexes are reported for mercaptobenzothiazol and dimethyldithiohydantoin (*43, 296, 300, 301*).

The actual nature of the electrode processes involved in the polarography of thiamine, vitamin B_1, is still not completely clear. Cathodic waves are observed for the unchanged compound in acid and neutral media (*345*). At a pH of 9 or higher the thiazole ring apparently opens and gives the thiol form of thiamine (*348*) which can give the anodic waves observed (*344*). The thiol form oxidizes easily to the disulfide form, which gives reduction waves at all pH values and a catalytic wave in cobalt solution at 65° or higher (*346*). A similar catalytic wave has been reported with natural and synthetic vitamin B_1 at room temperature (*131*) but not for oxidized vitamin B_1 (*221*).

In the determination of thiamine only vitamin C interferes and can be removed with potassium permanganate (*321*).

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Acid-Base Titrations in Nonaqueous Solvents

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AN INCREASE in the number of publications on the general subject of acids and bases has been noted during the past 2 years, accompanied by a greater interest in the analytical applications of nonaqueous solvents. Several publications, although not of recent date, but of general and specific interest, are included in the literature cited. These references, together with those given in the first review (*106*), should furnish a comprehensive index to the literature on the present concepts of acids and bases and their analytical application. Several excellent books have appeared. Some deal directly with nonaqueous chemistry (*4, 38*) and others with closely related subjects, parts of which are applicable to nonaqueous titrations (*33, 104, 129*).

Many suggestions have been made concerning the concept and definition of hydrogen and nonhydrogen acids. The term acid, as used here, includes all types of acids or the specific acid or acids under consideration. When it becomes necessary to differentiate the two primary categories, the terms H-acids and L-acids are used. The H-acids are those containing an ionizable hydrogen in water and are generally referred to as the Brønsted or Brønsted-Lowry acids. The L-acids are those that do not contain an ionizable hydrogen and are commonly referred to as Lewis acids. The term acetic acid refers to the glacial acetic acid in commerce. Descriptive adjectives such as anhydrous and dry are not used here in connection with solvents except ethyl alcohol. All solvents used are understood to be dry or substantially so.

THEORETICAL

The discussion here includes a variety of acid-base studies not readily classifiable otherwise.

Concepts of Acids and Bases. The concept of acids and bases is undergoing a continuous change. De Morveau states, "tenir la définition des acides, c'est tenir la clé de la Chymie" (*47*).

Mulliken (*96*) classified electron acceptors and donors into 25 types based on Lewis' broad conception of what should be meant by the words "acids" and "bases." Since the word acid is commonly used in a narrower meaning, he used an extension of Sidgwick's concept (*118*) of acceptors and donors. This classification makes it easier to treat under a unified scheme and viewpoint the action of one and the same donor molecules in such different activities as are expressed by

$$H_2O + BF_3 \rightarrow H_2O \rightarrow BF_3$$

and

$$H_2O + HCl \xrightarrow{aq} H_3O^+aq + Cl^-aq$$

H-acids, HQ, together with other molecules, RQ, are classified directly as acceptors in their own right along with primary Lewis acids, such as BF_3. This obviates the necessity of classifying H-acids as secondary L-acids as described by Luder and Zuffanti (*89*) which is essentially the proton transfer of Brønsted (*12*) and Lowry (*88*). It is believed that with the proposed classification of donors and acceptors into a number of fairly well-marked types, it may be worthwhile to attempt a roughly quantitative scale of donor and acceptor strengths for the interacting donors of a particular type with acceptors of a particular type. In discussing this study, Brown believed that the system will increase the ease of communication among specialists but will be a serious loss in communicating with workers in other fields of chemistry.

From a qualitative as well as a quantitative standpoint, Davis and Hetzer (*30*) concluded that the behavior of a base is a function of its environment. Based on spectrometric evidence (*29*), substituted guanidine-type bases react with a monobasic nonassociated acid, HA, in an aprotic solvent, such as benzene, in a manner as represented by the equations

$$\mathrm{R_3N + HA \rightleftarrows R_3NH^{+}_{\cdot\,\cdot}A^-} \quad (1)$$

$$\mathrm{R_3N + R_3NH^{+}_{\cdot\,\cdot}A^- \rightleftarrows (R_3NHNR_3)^+A^-} \quad (2)$$

A comparable sequence of reactions is proposed for the ionization of an acid and an amine in water

ACID

$$\underset{\text{base}}{\mathrm{H_2O}} \mathrm{{}+ HA \rightleftarrows H_2OH^+\ A^-} \quad (3)$$

$$\underset{\text{base}}{\mathrm{H_2O}} \mathrm{{}+ H_2OH^{+}_{\cdot\,\cdot}A^- \rightleftarrows (H_2OHOH_2)^+ + A^-} \quad (4)$$

$$(3) + (4)\ \mathrm{2H_2O + HA \rightleftarrows (H_2OHOH_2)^+ + A^-} \quad (5)$$

AMINE

$$\mathrm{R_3N + HOH \rightleftarrows R_3NH^{+}_{\cdot\,\cdot}OH^-} \quad (6)$$

$$\underset{\text{base}}{\mathrm{H_2O}} \mathrm{{}+ R_3NH^{+}_{\cdot\,\cdot}OH^- \rightleftarrows (R_3NHOH_2)^+ + OH^-} \quad (7)$$

$$(6) + (7)\ \mathrm{R_3N + 2H_2O \rightleftarrows (R_3NHOH_2)^+ + OH^-} \quad (8)$$

There is additional support for this formulation (*31, 32, 72, 82, 93, 144*). The primary reaction, Equations 3 and 6, provides a means of harmonizing the Brønsted and Lewis theories. In considering Equations 1 through 8, the proper measure of the reactivity of an acid in a nonionizing medium is the association constant for its reaction with some reference base (equation 1) and not a dissociation constant.

Ricci (*104*) proposed a different approach to hydrogen ion concentration, "...to consider the problem without special assumption and without dependence on theories of the mechanism of the process of ionization, but purely on the basis of mathematical definitions, and to prepare a systematic derivation of interrelated formulas for calculations involving the hydrogen ion concentrations in various aqueous solutions of almost any degree of complexity." The concepts presented appear to be applicable to the acetic acid system and to other systems comprising amphiprotic solvents and H-acids.

Gran (*50*) developed a method for determining the end point in a titration when the function $\Delta E/\Delta V$ is not definite. This method is similar to the one used in conventional conductometric titrations. It should prove of considerable assistance in nonaqueous titrations where $\Delta E/\Delta V$ is indistinct.

The entropy of ionization of protonic solvents has been measured in such systems as sodium acetate–water, sodium acetate–acetic acid, and sodium acetate–acetic acid solutions of perchloric acid (*63*). Gold and Hawes (*49*) studied the dependence of the degree of ionization of triarylmethanols on the composition of the medium in the ternary solvent system sulfuric acid–acetic acid–water and proposed a new acidity function, J_o.

Dielectric constant measurements were used by Giles, Rose, and Vallance (*48*) to study the interaction of phenols with amido and azo groups.

Kaufman and Singleterry (*66*) studied the reaction between tertiary amines and organic acids in nonpolar solvents. Tomíček and Heyrovský (*131*) reported rather extensive study of redox titrations in nonaqueous solutions. The titration of weak acids and their salts has also been discussed (*81*).

Strengths of Acids and Bases. Brown and coworkers (*13–15, 17–20*) studied the acid-base equilibria in gaseous systems where $\mathrm{B\!:\!A^3 \rightleftarrows B\!: + A}$ are simple reversible reactions. The bases are of the type $\mathrm{R_3N}$ where R = H or alkyl. The reference acid was trimethylboron. From the data, such thermodynamic quantities as ΔF, ΔH and ΔS may be determined readily. It is possible to compare the effects of different substituents in A and B. Such reactions are typical acid-base reactions and the relative strengths of the bases may be determined without the influence of solvent effect. It was established that

$$\mathrm{NH_3 < C_2H_5NH_2 \gg (C_2H_5)_2NH > (C_2H_5)_3N}$$

which is compared with the base strength in aqueous solution (*53*).

$$\mathrm{NH_3 < C_2H_5NH_2 < (C_2H_5)_2NH \gg (C_2H_5)_3N}$$

The strength of the methylamines was likewise determined and found to be $\mathrm{NH_3 < (CH_3)_3N < CH_3NH_2 < (CH_3)_2NH}$. To account for this observed order, they believe that steric hindrance or a steric factor plays a major role. If steric hindrance is the cause of the greater dissociation of triethylamine and hence its lower base strength compared to the standard reference acid, then if the three ethyl groups were tied together through the 2-carbon atoms, the resulting compound should be a stronger base than diethylamine.

Quinuclidine is, in effect, triethylamine in which the 2-carbon atoms are attached to a third carbon atom. This compound was prepared and found to be a stronger base when compared to alkyl halides than dimethylamine. From this and other data, Brown developed the F-, B-, I-strain theory of steric hindrance. The actual strength of bases could then be coordinated with the resonance theory. The ability of hindred amines, such as triethylamine, to react with aqueous acids is not noticeably affected because of the low steric requirement of the proton. Triethylamine in water is a much stronger base toward such acids as hydrochloric than it is in the gaseous state toward trimethylboron. However, Davis and Hetzer (*29*) pointed out that in water, as in other media, the proton does not have an independent existence.

The association constants of four bases, triphenylguanidine, triethylamine, diphenylguanidine, and di-*o*-tolyguanidine, were determined spectrometrically in benzene by their reaction with bromophthalein magenta E (*29*). The strengths in benzene were compared with their ionic dissociation constants, K_b, in water. The order of strengths of the three stronger bases appears to be an inverse relationship. On the basis of additional evidence from the literature, it is concluded that the order of strengths of a given group of bases in water is not a good guide to their strengths in an aprotic solvent like benzene, and that water and other similar amphiprotic solvents having a leveling effect on bases the same as they do on acids. The strength of bases and acids depends on the leveling effect of the solvent and the steric factors of the compound (*29*).

Everett (*37*) presents an interesting discussion on the problems related to the dissociation equilibria of acids and bases. The effect of a number of factors on the degree of ionization depends as much on the structure of the solvent as on the structure of the acid itself. Experimental results are interpreted in certain cases as functions of these factors.

Neutralization reactions in acetic acid were studied by Tomícek and Heyrovský (*130*). Their measurements were made with the hydrogen electrode. Methods of expressing strengths of acids and bases are discussed. Pifer and Wollish (*99*) found that the Fisher Senior Titrimeter could be used as a means of measuring the relative strengths of salts in acetic acid. The acid strength of iodine monochloride, antimony trichloride, and picric acid with reference to the bases pyridine and aniline in nitrobenzene have been determined (*79*). It has been shown from these and other data that the magnitude and in some instances the order of the strengths, of a series of acids in a given solvent depend on the base chosen as a reference and vice versa.

Cabannes (*24*) pointed out that the measure of the pH of liquids containing little water is inexact and further developed the proposals by Levasseur (*85*) for the corrected pH with these conditions called pHP = pH = $^1/_2 \log 55.5/[\mathrm{H_2O}]_x$, where $[\mathrm{H_2O}]_x$ is the molecular concentration of $\mathrm{H_2O}$ in the liquid studied. Examples of the usefulness of this conception are given. Smith and Elliott (*123*) measured the strength of several strong acids in acetic acid by the extent of reaction with a reference substance based on the acidity function H_o of Hammett and Deyrup (*54*).

Kilpi (*75*) presents a differential potentiometric method of measuring acid and base dissociation constants based on Van Slyke's general equation. A good pertinent bibliography is included. Healey and Martell (*55*) determined the conductivity at infinite dilution, dissociation constants of ion pairs, and ionic conductances at infinite dilution for several amines in 1,1-dichloroethane. The ionization constants of 38 amines were determined by means of liquid junction cells containing a hydrogen electrode immersed in a buffer mixture of the base and its salt. Attention is directed for the first time to the effect of two ethyl groups in enhancing the base strength (*53*).

Everett and Wynne-Jones (*36*) determined the dissociation constants of ammonium, methylammonium, dimethylammonium, and trimethylammonium ions in methanolic solutions containing 40% water. Brand, Horning, and Thornley (*11*) studied the ionization constants of aromatic nitro compounds in sulfuric acid and sulfuric acid and sulfur trioxide solutions. The nitrobenzenes are weak bases by their ultraviolet absorption spectra. Bell and Bayles (*8*) determined the basic strengths of some primary, secondary, and tertiary aliphatic and aromatic amines in anisole and chlorobenzene solutions by measuring their equilibria with 2,6-dinitrophenol and bromophenol blue. Gutbezahl (*51, 52*) discussed the acidity and basicity scale in the system ethyl alcohol–water in the correlation of acid dissociation constants.

Lemaire and Lucas (*84*) measured the constants pKa for several weak bases in glacial acetic acid and related pKa with the ionization constant. Brown and Brady (*16*) use the solubility of hydrogen chloride as a measure of the basic properties of the aromatic nucleus. Kilpatrick and coworkers (*69–71, 74*) studied the dissociation constants of acids in water and organic solvents. Kilpatrick and Luborsky (*73*) studied the base strengths of methyl-substituted benzenes. Hine and Hine (*61*) determined the relative acidities of water, methanol, and other weak acids in 2-propanol. Stewart and Cook (*125*) reported the basicity of aliphatic amines in water and ethyl alcohol. Additional information concerning the strength of acids and bases has been obtained by several authors (*107, 109–112, 114, 126, 137, 145*).

Corelli (*26*) reported that potassium hydrazide can be titrated to the acid color of Alkali Blau 6-B in alcohol with nitromethane. The reaction is not stoichiometric, and he states that it can be explained by the presence of a small amount of the aci-form. Bertin (*9*) studied acid-base reactions in mixtures of water, water–acetone, methanol, ethyl alcohol, and *p*-dioxane mixtures. Higuchi, Concha, and Kuramoto (*59*) were able to titrate very weak acids such as alcohols, acetanilide, and acetamide with lithium aluminum amide. This particular reagent does not react with the reducible functional groups that gave Higuchi and Zuck trouble when titrated with the lithium aluminum hydride (*60*).

L-Acids. Spandau and Brunneck (*124*) propose the following equilibrium in the thionyl chloride system:

$$SOCl_2 = SOCl^+ + Cl^- = SO^{++} + 2\ Cl^-$$

They investigated the solubility and conductivity of numerous compounds in this solvent. Antimony tri- and pentachlorides, ferric chloride, aluminum trichloride, stannic chloride, and sulfur dioxide react as acids. Substituted ammonium chlorides, amines, mercuric chloride, zinc chloride, and organic carbonyl compounds are bases. Titanium chloride and phosphorus pentachloride are amphoteric. Some acid-base indicators useful in aqueous systems may be used in thionyl chloride. Neutralization reactions were investigated by conductometric titrations. Sulfur dioxide acts as a strong base as follows:

$$2\ SO_2 + SOCl_2 = (SOCl)_2SO_3 = 2\ SOCl^+ + SO_3^{--}$$

Garber, Pease, and Luder (*45*) titrated aluminum chloride, stannic chloride, and aluminum tribromide with pyridine using crystal violet and malachite green as indicators in the thionyl chloride system. Aluminum tribromide was titrated with quinoline using crystal violet as indicator. Benzophenone is too weak a base in thionyl chloride to use as a standard; however, it can be titrated conductometrically.

Hein and Burkhardt (*56*) studied the reactions of triethanolamine derivatives of borate esters and showed that they form stable compounds with L-acids. Kolthoff, Stŏecsocá, and Lee (*79*) determined the strength of iodine monochloride and antimony trichloride with reference to pyridine and aniline in nitrobenzene. Rice, Zuffanti, and Luder (*105*) studied acid-base colors of eight indicators in several solvents with acids and bases as part of a program for investigating the quantitative titrations of L-acids. Herron (*58*) devised models illustrating the Lewis theory of acids.

SOLVENTS

Effect of Solvents on Relative Order of Acidity and Basicity. Hall and Sprinkle (*53*) found that the methylamines and ethylamines exhibit similar behavior—an increase in strength with the first alkyl substituent, a further increase with the second, followed by a sharp decrease with the third

$$NH_3 < CH_3NH_2 < (CH_3)_2NH \gg (CH_3)_3N$$

$$NH_3 < C_2H_5NH_2 < (C_2H_5)_2NH \gg (C_2H_5)_3N$$

Brown and Taylor (*19*) studied the gaseous systems of alkyl amines and trimethylboron and found that the strength of the methylamines was the same as in water. However, there was a marked alteration in sequence in the ethylamines

$$NH_3 < C_2H_5NH_2 > (C_2H_5)_2NH \gg (C_2H_5)_3N$$

With the more bulky reference acid, tri-*tert*-butylboron (*19*) there was a further change in sequence

$$NH_3 < CH_3NH_2 > (CH_3)_2NH \gg (CH_3)_3N$$

$$NH_3 > C_2H_5NH_2 \gg (C_2H_5)_2NH > (C_2H_5)_3N$$

The change in strength from the gaseous phase to the aqueous phase and from one reference base to another has been noted by other authors. Kolthoff, Stŏecsocá, and Lee (*79*) also have shown that the magnitude, strength, and order of a series of acids depends upon the solvent and reference base. Usanovich and Yatsimirskiĭ (*134, 135*) reported the order of increasing acidity for cations to be K^+, Na^+, Ba^+, Sr^{++}, NH_4^+, Pb^{++}, Li^+, Mn^{++}, Ca^{++}, Y^{+++}, Cd^{++}, Cu^{++}, Mg^{++}, Ni^{++}, Zn^{++}, Al^{+++}, and Be^{++} in acetic anhydride. Kolthoff and Willman (*80*) found the order to be Rb^+, K^+, NH_4^+ ($K^+ = NH_4^+$), Na^+, Li^+, Ag^+, Ba^{++}, Sr^{++}, Ca^{++}, and Mg^{++}. They reported on three acid ions in common and report the following acidities: Usanovich and Yatsimirskiĭ, I^-, NO_3^-, Cl^-, and Kolthoff and Willman, I^-, Cl^-; NO_3^-.

Davis and Hetzer (*30*) compared the strengths of 1,2,3-triphenylguanidine, triethylamine, 1,3-diphenylguanidine, and 1,3-di-*o*-tolylguanidine by plotting the log of dissociation constants in water against the log of the association constants in benzene. Among the three strongest bases, the basic strength appears to be reversed in the two solvents.

Leveling Effects. Shkodin, Izmailou, and Dzyuba (*115, 116*) concluded that the dissociation constants of bases in formic acid become level with weak bases, increasing their strength by tremendous amounts, and that inorganic acids remain strong and are not differentiated as in acetic acid. Organic acids such as acetic, monochloroacetic, trichloroacetic, salicylic, and picric acids are so weak in formic acid that they cannot be titrated. In a comparison of the strengths of substituted guanidines in water and in benzene, it was concluded that water has a leveling effect on the strength of bases as well as acids (*30*). The leveling effect produced by water and acetic acid on amines of markedly different strengths may be overcome if the titration is carried out in acetonitrile (*42*).

Mixed Solvents. There is considerable evidence that mixed solvents may be superior to a single solvent in general solvent power and in sharpness of the color change of indicators or in the potentiometric break. Pifer and Wollish (*100*) found that the sharpness of the potentiometric break is enhanced with an increase in concentration of *p*-dioxane in the acetic acid system. The *p*-dioxane is most conveniently added as the solvent component of the titrant. A slight increase in sensitivity was noted with $0.1N$ perchloric acid in *p*-dioxane. The increase in sensitivity becomes marked with $0.01N$ perchloric acid in *p*-dioxane. A series of five potentiometric titrations was made by dissolving 2-dimethylamino-6-(β-diethylaminoethoxy)benzothiazole in acetic acid and *p*-dioxane so that the final titrating solution contains 0, 29, 43, 57, and 86% *p*-dioxane. No distinguishing break in the titration curve for the first equivalent was observed in the system containing 0% *p*-dioxane. Pifer, Wollish, and Schmall (*102*) further demonstrated that striking changes in sensitivity may be had in acetic acid by adding solvents of low dielectric constant which sharpens the end point in many cases.

Fritz (*42*) pointed out that butylamine and pyridine cannot be differentiated when titrated in water or in a system containing an appreciable amount of acetic acid. The two bases could be differentially titrated when dissolved in acetonitrile and titrated with perchloric acid in *p*-dioxane.

Thiers (*128*) studied the titration of about 75 materials in 95% ethyl alcohol with $0.1N$ aqueous sodium hydroxide or hydrochloric acid. He concluded that water added during the titration tends to flatten the buffer region, thereby sharpening the end point.

General. Monk (*94*) studied the influence of mixed solvents on the solubility of salts in water–methanol, ethyl alcohol, acetone, 1-propanol, ethyl acetate, *p*-dioxane, 1,2-ethanediol, and glycerol systems and concluded that the value of R is characteristic of the organic solvent component rather than the salt. Dimethylformamide is used as the solvent for the more acidic sulfonamides and butylamine for the more weakly acidic ones (*43*). Fritz (*44*) recommends that phenols with negative substituents be titrated in dimethylformamide where phenol and alkyl substituted phenols are weak acids and can be titrated in ethylenediamine. Differential titration of phenols and carboxylic acids can be made in either acetone or acetonitrile. Ethylenediamine and dimethylformamide were used as the solvent for the titration of enols and imides (*40*).

Burg and McKenzie (*22*) reported studies with nitrosyl chloride as an ionizing solvent. Kipling (*77*) found that monomeric acetic acid forms H-bonds with water to form a hydrate which forms a dimer with itself. Little or no free acetic acid exists in the presence of water. Leader and Gormley (*83*) determined the dielectric constants at 10 mc. and the temperature range 15° to 35° C. for pure liquid *N*-methylamides. Davies and Monk (*28*) studied the influence of solvents on the dissociation constant of silver acetate by measuring the solubility of silver bromite in solvent mixtures with methanol, ethyl alcohol, acetone, 1,2-ethanediol, *p*-dioxane, and glycerol. Thionyl chloride in nitrobenzene was used as the solvent for titrations of L-acids (*45, 79, 124*). Barnham and Clark (*6*) studied the decomposition of formic acid at low temperatures.

Purification of Solvents. Most of the solvents used in nonaqueous titrations are grades available from suppliers and many are used as received. Often the solvent will be brought to the potentiometric or indicator equivalent point with the titration before adding the sample. One of the disadvantages of *p*-dioxane as a solvent for perchloric acid is that the solution becomes colored in a short time. The amount of coloration often is great. The *p*-dioxane can be purified by distilling from sodium, passing through an adsorption column, and by shaking with Amberlite IRA 400 (OH) resin and filtering (*103*). Sideri and Osol (*117*) found that if 20 grams of asbestos (type used in preparing filter pads) were shaken with 1 liter of *p*-dioxane for an hour or two and filtered through a pad of asbestos, no coloration occurs when the perchloric acid solution is prepared.

Characterization of Chemicals. The evaluation of some studies is difficult because the authors fail to characterize precisely their solvents and reactants. Patterson (*98*) presents a valuable series of qualifying terms used for general purity classification when analytical characterization has not been made.

TITRANTS

Pyridine, quinoline, and benzophenone were used to titrate L-acids in thionyl chloride (*45*). Fritz and coworkers used sodium methoxide in a mixture of benzene-methanol, 4 to 1 v./v., as a titrant in a number of systems (*40, 41, 43*). Perchloric acid in *p*-dioxane has been shown to be superior to perchloric acid in acetic acid as a titrant (*100*).

Burg and Campbell (*21*) reported the preparation of a new boron base, $Na_2HB(CH_3)_2$, with characteristics that may make it valuable as a titrant in nonaqueous solvents. Higuchi and coworkers (*59, 60*) found that lithium aluminum hydride and lithium aluminum amides can be used for the titration of very weak acids.

INDICATORS AND ELECTRODES

Tomíček's book (*129*) is primarily concerned with the use of indicators in aqueous solutions but contains useful information that is applicable for the use of indicators in nonaqueous media. King (*76*) presents a study of the factors affecting the selection and use of indicators.

De Ment (*33*) presents a brief discussion of advantages, limitations, and applications of fluorescent indicators for aqueous solutions. Of particular interest is a list of 63 fluorescent indicators arranged for each unit of pH from 0 to 14. Many of these indicators should also be applicable to nonaqueous titrations. Tomíček and Suk (*132*) reported some neutralization fluorescence indicators and their pH ranges in water.

Electrodes. Sease (*113*) discusses electrometric titrations in general terms with particular reference to their disadvantages and applicability. Tomicek and Heyrovsky (*130*) used the hydrogen electrode covered with palladium black in their study of reactions in acetic acid. It was found that antimony and tellurium electrodes as well as glass electrodes, blown from various samples of glass, do not give correct results in relation to concentration. The quinhydrone and chloranil electrodes cannot be used in acetic acid containing acetic anhydride.

The quinhydrone-calomel electrode system was used to measure the strength of bases in formic acid (*115*). Bishop (*10*) reports that the glass, antimony, and platinum electrode can be used as reference indicator electrodes and the silver reactor electrode can be used in dry ethyl alcohol for argentometric titration. Levin (*87*) reports on the reproducibility of the antimony electrode.

Conductometric and High Frequency Titrations. Wagner and Kauffman (*140*) demonstrated that titrations may be carried out in acetic acid using a high frequency system. Ishidate and Masui (*62*) titrated weak acids with sodium methylate in benzene-methanol mixture using high frequency. Conductometric titrations were used for the thionyl chloride system in titrations with L-acids (*45, 124*).

Indicators. Eosin Y and methyl violet were used in the differential titration of aromatic amines in acetonitrile. *p*-Nitrobenzeneazoresorcinol (azo violet), *o*-nitroaniline, and thymol blue were used in ethylenediamine and dimethylformamide for the titration of imides and enols (*41*). Thymol blue and azo violet were found to be suitable indicators for the titration of amine salts of organic and inorganic acids in several basic solutions with sodium methoxide in benzene-methanol (*42*).

Ekeblad (*35*) mentions the use of BZL-Blau (Ciba 22062) for strong bases and neutral red and Nile blue sulfate for weak bases in the acetic acid system. L-acids were titrated in the thionyl chloride system using malachite green and crystal violet (*45*).

METHODS

The acetic acid system is still the most universally used of the nonaqueous systems. The use of mixed solvent systems has been shown to be superior for many substances since the last review. During the past 2 years, the emphasis has been on types of analysis more than on exploration in various solvents. The most extensive study in the nonaqueous media has been in the field of pharmaceuticals. Many pharmaceuticals, amines, imides, and other nitrogen-containing compounds and their salts are readily titratable in nonaqueous media. Pifer, Schmall, and Wollish (*103*) in their review of titrations of pharmaceuticals in nonaqueous solutions stated, "the field of nonaqueous titration offers a variety of possibilities for the assay of pharmaceutical compounds, many of which cannot be determined readily by other methods." The importance of nonaqueous titrations to the pharmaceutical field is summed up in the following attributes: specificity, solubility, simplicity, sensitivity, selectivity, accuracy, and precision. They have developed two effective extraction apparatus for extracting the active ingredients from an aqueous phase to a nonaqueous phase for subsequent titrations (*108*).

Mixtures of Acids and Acid Anhydrides. Siegel and Moran (*119*) in their study of esterification rates of dibasic acid anhydrides used a combination of aqueous and nonaqueous titrations to determine the acid and anhydride content of the mixture. Aqueous titration results in the hydrolysis of the anhydride and titration of both constituents as dibasic acids. Titration with alcoholic alkali results in titration of the acid as a dibasic acid. The alcohol immediately forms the monoacid ester with the anhydride which simultaneously titrates as a monobasic acid. The alkali catalyzes the ester formation and the speed is almost instantaneous.

Garrett and Guile (*46*) use the basic technique (*119*) in their determination of the maleic anhydride–styrene copolymers. Potentiometric titration of the polymer in acetone with methanolic sodium hydroxide was superior to aqueous titration with phenolphthalein (*119*). The indicator was absorbed on the copolymer and the end point was difficult to obtain. It was found that the methanolic sodium hydroxide potentiometric end point coincides with the stoichiometric point of aqueous neutralizations of one half of the total potentially available carboxyls. Nicolas and Burel (*97*) further studied these determinations.

Siggia and Hanna (*121*) studied the method of Malm and Nadeau (*90*) for determination of acetic anhydride in acetylating mixtures for cellulose and found that it could be applied to the determination of other carboxyl anhydrides in the presence of their acids. Propionic, maleic, phthalic, camphoric, and butyric anhydrides were analyzed. The accuracy and precision are good.

Siggia and Floramo (*120*) determined free maleic and phthalic acids in their anhydrides. The method is based on the fact that tertiary amines do not react with the anhydrides. The two strongest amines found suitable for the purpose were tripropylamine and *N*-ethylpiperidine. The sample was dissolved in dry acetone or 2-butanone and potentiometrically titrated with a base. The method is limited to acids of an aqueous strength of 10^{-3} or greater. Only acids of equal or greater strength will interfere.

Anastasi, Mecarelli, and Novacic (*2*) titrated isonicotinic acid hydrazide with sodium methylate in dimethylaniline to the thymol blue end point.

Halides. It has been demonstrated that a large variety of salts, both metallic and nitrogenous, could be titrated in acetic acid with perchloric acid (*91*). Many of the more useful salts in pharmaceutical preparations and in industrial processes are concerned with the halides. These salts are not titratable in acetic acid because halide acids are too strong in this solvent to be sufficiently titrated with perchloric acid (*80*).

In considering the base strength of inorganic acetates and the strength of cations in acetic acid as determined by Kolthoff and Willman (*80*), Pifer and Wollish (*100*) surmised that mercury(II) acetate would react with the halogen ions to form a lowly ionized mercury(II) halide. This would remove the halogen ion from solution. The excess mercury(II) acetate would not interfere with the titration, since it was lowly ionized. The surmise was correct and presented a means of analyzing the halides. The use of mercury(II) acetate converts the halide salt to the acetate which is the strongest base form in acetic acid. The method is simple, rapid, and accurate. It may be used with visual indicators and in potentiometric titrations. The titrant used was perchloric acid in *p*-dioxane, 0.01 or $0.1N$.

No effect on the potentiometric end point was observed when the titration was run at room temperature or in hot solutions. A large excess of mercury(II) acetate, up to 3 grams, showed no deleterious effect with $0.1N$ perchloric acid. When $0.01N$ perchloric acid is used, the mercury(II) acetate should not exceed 2 moles per mole of the compound being titrated. For most compounds, the visual end point was not found to be sufficiently sharp when titrated with $0.01N$ perchloric acid. Good results were obtained with potentiometric titrations.

Solvents commonly used in pharmaceutical preparations such as ethyl alcohol, 2-propanol, glycerol, 1,2-propanediol, and Carbowax do not interfere. Water interferes with the sharpness of the end point when present to the amount of 1%. Almost all cations other than mercury(II) will interfere with the titration. Organic and inorganic acids (except strong acids in acetic acid) do not interfere. A large number of pharmaceutical-type halogen compounds were titrated including amines, heterocyclic nitrogen salts, vitamins, and quaternary ammonium salts.

With the same technique and titrant the method was extended to inorganic salts (*99*). The sodium salts of 29 different inorganic anions were titrated. The following sodium salts had not been previously reported: azide, bromate, chlorate, cyanide, chloride, hypophosphite, iodate, iodide, molybdate, nitrite, nitrate, primary, secondary and tertiary phosphate, sulfate, thiocyanate, and tungstate. It is stated that the aluminum, ammonium antimony, barium, bismuth, cadmium, calcium, cobalt(II), iron, lead, magnesium, manganese(II), potassium, silver, strontium, and zinc salts of the 29 anions may be successfully titrated, provided they can be solubilized in acetic acid. The method for determining the acidic or basic reaction in acetic acid is given.

Choline salts of carboxylic acids may be determined in acetic acid with perchloric acid in acetic acid as a titrant with either potentiometric or indicator titrations (*92*). No deleterious effect was observed if the solution contained 3% or less of water. The reaction of perchloric acid with choline salts is stoichiometric. Solvents such as ethyl acetate, ethyl ether, acetonitrile, acetone, *p*-dioxane, nitromethane, benzene, and carbon tetrachloride do not interfere when present to 10% of the volume of the original titrating medium. Trimethylammonium carboxylic acid salts, if present in the choline preparation, will be titrated. The presence of volatile amine salts can be determined (*27*). Aqueous choline solutions containing as much as 90% water can be assayed by adding sufficient acetic anhydride to the sample in acetic acid to react with the water and very gently boiling the mixture for 5 minutes. The method is very precise.

Choline chloride may be determined by the mercury(II) acetate modification (*100*). Pifer and Wollish (*101*) studied the analysis of thiamine salts and found that thiamine mononitrate can be titrated with perchloric acid in dioxane–acetic acid system and that the hydrochloride can be titrated by adding mercury(II) acetate (*100*). Levi and Farmilo (*86*) analyzed amine–cadmium halide complexes by modification of Pifer and Wollish's method (*99*). The amines and cadmium halide from which the complexes were made were analyzed by the method of Fritz (*39*) and Pifer and Wollish (*100*).

Tomiček and Zukriegelová (*133*) potentiometrically and visually titrated lithium chloride and bromide in acetic acid with $0.1N$ mercury(II), lead, and thallium acetates in acetic acid. Potassium nitroprusside and dithizone were used as indicators for the mercury(II) acetate titration. Neutral red, thionine, and safranine were used for the thallium acetate titration. Reversed titrations of thallium and mercury(II) acetates with thallium chloride and bromide were carried out potentiometrically.

Fritz (*41*) studied the titration of organic nitrogen salts in several solvent systems. The salts studied were sulfates, benzoates, hydrochlorides, iodides, citrates, perchlorates, and picrates in the solvent systems water-ethylenediamine, water-morpholine, ethylenediamine, and dimethylformamide using azo violet or thymol blue and sodium methoxide in benzene-methanol, 1 to 1 v./v. as the titrant. He demonstrated that a wide variety of substances can be analyzed.

Amines. Keen and Fritz (*68*) studied the microtitration of amines with perchloric acid in acetic acid. Solvents used were acetic acid and chlorobenzene. They report that acetonitrile, benzene, carbon tetrachloride, chloroform, 1,2-diethoxyethane, ethyl acetate, 1,2-dichloroethane, and nitrobenzene titrations were made using methyl violet and potentiometric methods. Diphenylguanidine and potassium acid phthalate were used as standards. The amines were high purity commercially available material, and the precision was good. The leveling effect produced by water and acetic acid on amines of markedly different strengths can be overcome if the titration is carried out in acetonitrile.

Fritz (*42*) differentiated between the sharp breaks in aromatic and aliphatic amines such as butylamine and pyridine, ethanolamine and aniline, and the aromatic and aliphatic amine compounds in cinchonine. He obtained sharper breaks than Wagner, Brown, and Peters (*139*) when the primary amine is converted to the azomethine with salicylaldehyde.

Kleckner and Osol (*78*) analyzed antihistamine bases and their salts by the method of Pifer and Wollish (*100*). Terry, Kendrick, and Moe (*127*) titrated fatty amine products of high molecular weight in acetic acid. Shkodin, Izmailou, and Dzyuba (*115*) titrated such weak bases as theobromine and caffeine in formic acid with $0.2M$ p-toluenesulfonic acid. Butler and Ramsey (*23*) analyzed p-aminosalicylic acid and the sodium salt by titrating with perchloric acid in acetic acid. The titration media was a mixture of acetic acid and carbon tetrachloride. Vespe and Fritz (*138*) determined barbiturates and sulfa drugs in pharmaceutical preparations by titrations in dimethylformamide with $0.1N$ sodium methoxide with thymol blue indicator.

Alicino (*1*) titrated isonicotinic acid hydride in acetic acid with perchloric acid using crystal violet and potentiometric titrations. The accuracy (assuming 100% from elemental analysis) and precision were good. Fritz and Keen (*43*) titrated sulfonamides in dimethylformamide with thymol blue indicator and in butylamine with azo violet indicator with sodium methoxide in benzene-methanol mixture. Butylamine enhances the acid strength of sulfonamides more than dimethylformamide and is therefore used to titrate the more feebly acidic sulfonamides.

Keen (*67*) reports a rapid control method for determination of amines in hydrocarbon polymerization feed. The feed gases are condensed; 5 ml. of $0.02N$ perchloric acid in 1,2-diethoxyethane is added and the hydrocarbon condensated refluxed away. The excess acid is titrated with diphenylguanidine in the same solvent. Moore, McCutchan, and Young (*95*) electrometrically and differentially titrated pyridines from pyrroles in shale oil distillates with perchloric acid in acetic acid. Ward, Moore, and Ball (*141*) extended this work and developed an analytical scheme for determination of types of nitrogen compounds in petroleum distillates based on a combination of methods for total nitrogen, basic nitrogen, and pyrrole nitrogen.

Veibel, Eggerson, and Linholt (*136*) titrated pyrazolones in acetic acid with perchloric acid. Those pyrazolones that can establish a pyrazole structure by shifting of a H from C_4 to N_2 or to O at C_5 can be titrated. Basu (*7*) determined the molecular weight of nylon dissolved in phenol by titration of the end group with perchloric acid in 1,2-ethanediol and 2-propanol. Heiz (*57*) titrated barbituric acid derivatives potentiometrically in pyridine with the glass-antimony electrode system. Thymol blue and phenolphthalein can be used. Washbrook (*142*) determined the neutralization and saponification values of used lubricants.

Alcohols and Phenols. Fritz and Keen (*44*) titrated phenols in dimethylformamide and ethylenediamine with potassium methoxide in benzene-methanol with p-nitrobenzeneazoresorcinol (azo violet) and o-nitroaniline as indicators. Certain carboxylic acids and phenols were differentially titrated in acetone. It was also shown that most phenols with negative substituents can be titrated in dimethylformamide using azo violet indicator. Alkyl substituted phenols and some weak acids can be determined in ethylenediamine using o-nitroaniline as indicator. In either acetone or acetonitrile, carboxylic acids can be determined in the presence of most phenols using p-hydroxyazobenzene as indicator. Higuchi, Concha, and Kuramoto (*59*) found that lithium aluminum amides were more satisfactory titrants for very weak acids than lithium aluminum hydride. Katz and Glenn (*65*) determined phenols in coal hydrogenation oils. The sample was dissolved in ethylenediamine and titrated with sodium aminoethoxide.

Ketones and Aldehydes. Siggia and Segal (*122*) utilized the Schiff base reaction of the primary amine and aldehyde for the determination of aldehydes. Only aliphatic amines may be used. was found that lauryl amine in 1,2-ethanediol and 2-propanol mixtures was a satisfactory reagent. The amine is added to the aldehyde and the excess amine is titrated potentiometrically with salicylic acid in the same solvent with the glass-calomel electrode system. The accuracy reported is good. Acids stronger or nearly as strong as salicylic acid interfere, as do acid anhydrides and acid halides.

L-Acids. Garber, Pease, and Luder (*45*) successfully titrated tin(IV) chloride and aluminum chloride and bromide in thionyl chloride with pyridine using crystal violet and malachite green as indicators. Aluminum bromide was titrated with quinoline with crystal violet as the indicator. Tin(IV) chloride was titrated conductometrically with benzophenone.

Imides and Enols. The scope and the limitations of the titration of imides and enols as acids in nonaqueous media are discussed (*40*). Compounds having the configuration A—CH_2—A or A—NH—A′ can be titrated in dimethylformamide or ethylenediamine if A and A′ are carbonyl groups or any of several other groups possessing electron-withdrawing properties. Sodium methylate is used as the titrant with thymol blue, azo violet, or o-nitroaniline as the indicator depending on the acidic strength of the compound to be titrated. In the absence of other acidic compounds, the method is accurate and rapid. Interfering substances include acids, phenols, amine salts, and active halogens.

Hydrazines of pyridinecarboxylic acids were titrated in acetic acid with perchloric acid (*64*).

REVIEWS AND BOOKS

Pifer, Wollish, and Schmall (*103*) prepared a review of titrations of pharmaceuticals in nonaqueous solvents. The importance of titrations in nonaqueous solutions to the pharmaceutical field they attributed to the following qualifications: specificity, favorable solubility, simplicity, sensitivity, selectivity, accuracy, and precision. This is an excellent well documented review on practical methods and their application. Auerbach (*5*) presented to the U. S. Pharmacopoeial Convention Conference a limited review of titrations in nonaqueous solvents with special reference to acetic acid together with his experience on work in this field. He discussed some of the applications to analysis of pharmaceuticals and advocated its use in pharmaceutical assays. Several other reviews were prepared (*3, 25, 35, 47, 143*).

Fritz (*38*) has compiled in a booklet a brief discussion of the acid and base theories. The larger part of the book is concerned with procedures. This book is recommended to those wishing to use the methods available up to early 1952. Audrieth and Kleinberg's book (*4*) "Non-Aqueous Solvents," although it is not primarily concerned with analytical chemistry, contains a wealth of correlated and evaluated information valuable to the analytical chemist working in nonaqueous media. The first two chapters, covering properties of solvents and acids and bases, clearly and simply present a concept of the solvent in relation to chemical analysis. Much of the material presented in this book normally would be missed in a literature survey of nonaqueous solvents.

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Potentiometric Titrations

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THIS paper attempts to summarize the chief trends in the development and application of titration methods that are essentially potentiometric. The period covered begins with the time of preparation of a prior review of the subject by the author (*67*).

THEORETICAL DEVELOPMENTS

Polarization Curves and Electrotitration Methods. A much clearer idea of the fundamental principles and the interrelations of various electrotitration processes has resulted from work from a few active centers during the period 1951 to 1953. Clarification has resulted in the main through theoretical and experimental study of polarization curves and a much clearer understanding of the phenomena that are involved in indication processes.

The most extensive theoretical treatment of polarization curves as related to electroanalytical methods is due to Gauguin and coworkers Charlot, Bertin, Badoz-Lambing, and Coursier in France. Their papers deal with general relations (*72*, *75*), potentiometry at a small constant current (1 to 5 μa.) (*14*, *71*, *74*), interpretations of potential measurements (*42*), coulometry at constant current (*73*), and amperometry at constant e.m.f. (*8*, *14*, *76*). Polarization curves are considered in terms of "ideal electrolysis," where current density, at an anode, for example, is given by:

($i = kn_TF\,(\text{Red})e^{\frac{\beta nF}{RT}E}$), k being a constant depending upon choice of potential origin, (Red) the activity of the reductant, n_T total number of electrons per molecule of reductant in the electrode process, and n the number of electrons in the slowest intermediate stage—i.e., $n < n_T$. β is the transfer coefficient. With the aid of equations of this type for the various oxidants and reductants, and polarographic diffusion expressions, mathematical expressions are derived for anodic, cathodic, and mixed anodic-cathodic polarization curves for reversible and irreversible oxidant-reductant systems or for mixtures of such systems, both reversible and irreversible. The position of the polarization curves along the applied voltage axis is important in determining the magnitude of the e.m.f. change that is produced at the end point at small constant applied current.

Reilley, Cooke, and the writer (147) developed a three-dimensional model that is useful in understanding the ideal relationships between polarographic $E\frac{1}{2}$ values and polarographic waves, current, and ratios of oxidant and reductant concentrations, in reversible systems. This model shows clearly the relation between potentiometric and amperometric titrations and polarography. By considering planes of currents slightly above and below zero—e.g., 1 to 2 μa.—the possibility of derivative relationships leading to potentiometric changes at end points is easily seen. The relationships are more clearly visualized from polarization curves (*146*). Because data are needed with various media and various sizes and shapes of electrodes both for medium alone and with oxidant and reductant systems, a current-scanning technique was developed by Adams, Reilley, and the writer (*5*) and found to be much more rapid and convenient with solid electrodes than making a voltage scan. Time maxima do not occur with current as the controlled variable. These curves in actual situations are of great value both for studying new titrimetric possibilities and for coulometric studies. Delahay (*46*), as well as Gauguin *et al.* (*74*) and Badoz-Lambing (*8*) also realized clearly the importance of polarization curves to the coulometric titration methods. With an efficient technique (*5*) it is possible to find out rapidly whether a coulometric reagent may be generated at an adequate approach to 100% efficiency in the medium desired and with the particular size and shape of electrode and current density that one intends to use.

Duyckaerts (*53*) has also considered the bearing of polarization curves upon methods involving constant current or constant voltage between electrodes. He developed (*54*) a theoretical treatment that has much in common with the work of Gauguin and associates and the author's studies. His equations are developed from the standpoint of the rate theory of Eyring and associates—for example, for an irreversible system with oxidant and conjugate reductant present:

$$i = k_1\,(\text{Ox})\,e^{\frac{-\alpha nF}{RT}E} - k_2\,(\text{Red})e^{\frac{(1-\alpha)nF}{RT}E},$$

where k_1, k_2 are rate constants and α is a coefficient of activation. His treatment for a reversible system reduces to the classical polarographic equation. He has stated clearly the relation between the various electrometric methods and also considers the bearing of constant resistance on electrometric methods.

Kambara *et al.* (*100, 189*) have examined the theory of the diffusion current at the rotating platinum electrode and have concluded that the current-voltage equation or diagrams are essentially similar to those for a mercury electrode.

Potentiometry at Constant Current Density. DERIVATIVE POLAROGRAPHIC TITRATION. The subject of potentiometry at constant current density has been developed (*74*) both for systems consisting of a reference electrode and an indicator electrode and for two similar indicator electrodes. The latter process is identical with the method that the author's group has called "derivative polarographic titration" (*146*). With dissimilar electrodes there is a strict limitation in the amount of current that can be passed. This newer field of potentiometric titration will become a very useful supplement to preexisting methods.

Dead-Stop Method. AMPEROMETRY AT CONSTANT POTENTIAL. The chief differences of opinion between the authors of recent articles on this topic appear to arise from lack of definition as to what is a "small" applied e.m.f. As originally proposed by Foulk and Bawden (1926), the applied e.m.f. was designated as 10 to 15 mv. If this definition is adhered to, very many of the later applications that have been classed as dead-stop titrations deviate more or less markedly in the nature of the end-point indication and are very clearly of amperometric titration nature, in the sense that a very large e.m.f. between electrodes must be applied in order to cut the polarization curves from various concentrations of an oxidant or a reductant. Stone and Scholten (*170*) have used applied voltages from 0.05 up to 0.4 volt. All these methods approach forms of "amperometry at constant potential" (*76*).

Delahay (*45*) interpreted dead-stop phenomena at 10 mv. applied e.m.f. in terms of polarization curves of reversible and irreversible systems. The latter type of system may show anodic and cathodic overvoltages so great that no electrolysis can proceed at the small applied potential. If a reversible system appears at the end point, an appreciable current can pass at the e.m.f. applied. An increase in the applied e.m.f. can eventually cause an irreversible system to pass current. The electrolytic process at one electrode may not be the reverse of the process at the other electrode. Stone and Scholten (*170*) found that nitrite in diazotation reactions at 0.4 volt applied yields nitric oxide at the cathode and nitrogen dioxide at the anode.

Stock (*169*) has reviewed dead-stop applications. Bradbury (*26*) has given a thorough general discussion of the method in terms of overpotential effects (activation overpotential, concentration overpotentials) and *IR* drop and diffusion phenomena. The various cases of irreversibility of one or both systems and indicator phenomena at attackable electrodes are also discussed.

Gauguin and Charlot (*73*) and Duyckaerts (*53*) have pointed out that in amperometry at constant potential a reversible system gives a curve of current *vs.* milliliters of reagent rising to a rounded maximum at the midpoint, followed by a fall almost linear near the end point, followed by a sharp rise if a reversible system is present beyond the end point, or almost zero current if there is no process reversible at both electrodes. The reverse-type of graph is also possible. Kiess (*106*) and Stone and Scholten (*170*) have also published curves of this character.

Duyckaerts (*53*) and Gauguin and Charlot (*75*) have pointed out that "potentiometry at constant current and amperometry at constant potential either with reference electrode and indicator or with two indicator electrodes are both limiting cases of a more general method which one would call potentiometry or amperometry at constant resistance." When the sum of the series and solution resistances is very large and e.m.f. applied is very small, potentiometric conditions prevail. If e.m.f. applied is very large, the current is small (constant) and end points may be found by potential changes. If the sum of the resistances is small, e.m.f. applied may remain constant and changes in current are easily measured.

Bordoni (*25*) and Oelsen *et al.* (*136*) have pointed out that variation in behavior of an indicator electrode that is polarized by a suitably chosen attackable electrode may be used for indication. This type of procedure is fairly familiar in the amperometric titration field.

Theory of Equivalence-Point Potentials and Equilibria. Bishop (*22*) has pointed out that in cases where all the coefficients in a redox reaction are different, $a\text{Ox}_1 + b\text{Red}_2 = c\text{Red}_1 + d\text{Ox}_2$, calculations of equilibria are difficult or impossible unless $a + b = c + d$. Ohlweiler (*138*) has discussed the theory of the equivalence point and the completeness of the reaction in redox reactions.

Gran (*80*) has advocated the plotting of potentiometric titration data in linear form by using expressions such as $(V_0 + V)\,10^{K_1 - \text{pH}} = K_2\,(V_e - V)$, where K_1, K_2 are constants containing activity coefficients and V_0, V_e, and V are, respectively, initial volume, volume at the equivalence point, and volume of reagent added at any point. A similar equation with appropriate constants applies beyond the end point. Similar expressions are given for other types of titrations. The process may be simplified by plotting points corrected for volume changes on logarithmic paper.

APPARATUS

Automatic Titration. Frediani (*60*) developed a special apparatus now commercially available (Beckman Co.) for the dead-stop titration as applied in the determination of water by the Karl Fischer method. A time-delay switch preadjusted for any time up to 1 minute prevents false end points due to the slow yielding of water from suspended matter. Titration is automatically resumed if the electrodes drift back within the preset interval.

Carson (*35*) developed an automatic apparatus for coulometric titration and also (*36*) a circuit that gives automatic titration to an end point with a portion of the solution reserved in a side tube. At this point a piston operated magnetically forces the reserved solution into the main vessel and the titration is resumed automatically at a slow rate until the true end point is reached. Other automatic titrators have been described by Juliard and van Cakenberghe (*99*), Dunn *et al.* (*51*) (dual assembly for aqueous and nonaqueous media), Saeki (*154*), Wise (*196*), and Fowler *et al.* (*59*). The last is a combined robot titrator and dispenser capable of 100 titrations per hour.

Several pH meters and vacuum-tube voltmeters have been described by Takaki *et al.* (*174*), Ishibashi *et al.* (*94*), Champaygne (*37*), and Anderson and Greenwood (*6*). DuBoff and Pratt (*49*) have described a selector switch for use with a glass electrode and several electrodes of other types dipping in the same solution.

Modified cells for the Karl Fischer titration have been developed by Campbell (*33*) and by Menville and Henderson (*122*).

Collier and Fricker (*40*) describe a convenient switching arrangement to shift from series to parallel positioning of the galvanometer in dead-stop titrations. Morpain and Trenchant (*128*) describe a semiautomatic buret for use with the dead-stop method.

The arsenic electrode has been proposed for acid-alkali titrations by Mousa (*129*). Bishop (*20, 21*) has studied the use of electrodes that eliminate salt bridges in various types of titrations—for example, the glass-antimony electrode pair serves in the titration of halides and thiocyanate with silver ion. The antimony electrode is changed by plating out silver just beyond the end point. The glass-silver pair indicates well in iodometric titrations.

Takagi and Shimizu (*172*) have explored the use of tantalum—tantalum pentoxide as indicator in acidimetry, tantalum-graphite in iodometry, tantalum-tungsten in ferrocyanide reactions and in titration of sulfide ion with mercuric, and tantalum-platinum for titrations with silver nitrate. Banchetti (*10*) found that the platinum-Nichrome pair served in acid-base titrations if hydrogen peroxide was added. Giunta (*77*) used similar electrodes with one shielded by solution contained in space with porous connection to the solution titrated. Chilton *et al.* describe a simple conventional assembly for potentiometric titration (*38*).

Kamienski (*101–103*) has investigated the use of various electrodes sealed into chromatographic columns for detecting the passage of ions such as copper. He termed this process potentiometric chromatography.

Cooke, Reilley, and the writer (*41*) have found that the opposed e.m.f. method of Erich Müller—i.e., equal and opposite to equivalence point potential—is one of the more sensitive indicating devices for coulometric estimations in the microgram range. The indication is essentially amperometric in character.

Parks and Lykken (*140*) have stressed the application of potentiometric, amperometric and polarographic methods in microanalysis.

APPLICATIONS

Determination of Constants. Grunwald (*83*) has used a differential potentiometric method to derive ionization constants of acids and bases. Grunwald and Berkowitz (*84*) used this process for estimating pK_a values in ethyl alcohol–water mixtures. Kilpi (*107*) advocates the differential process in the buffering region rather than as Grunwald applied it near the equivalence point.

Potentiometric acid-base titration has long been used for estimating the stability constants of complexes. Freiser *et al.* (*63*) have employed the Bjerrum-Calvin procedure for estimating the stabilities of metallo-organic chelates. Schwarzenbach (*160*) has summarized the application of some of his numerous researches on chelates as a basis for titration processes.

Geloso and Deschamps (*76*) have estimated solubilities of basic salts by measuring pH and fraction precipitated. Meites (*121*) determined the solubility product of copper mandelate by potentiometric titration of a suspension of the salt with perchloric acid.

Acid-Base Processes. Dubois and Walsich (*50*) have applied the dead-stop technique to acid-base titrations. Cuta and Valebil (*44*) have reinvestigated the titration of hydroxide-carbonate mixtures.

The microtitration of a single small drop of fatty acid solution in controlled atmosphere with $0.001N$ potassium hydroxide is described by Grunbaum, Shaffer, and Kirk (*82*). The alkali is produced by passage of standard potassium chloride solution through hydroxyl-charged anion exchange resin.

Oelsen and associates (*134–137*) have applied potentiometric methods to the determination of acids, bases, and carbon in inorganic and organic compounds. Carbon dioxide was absorbed in excess barium hydroxide and the amount absorbed was found by back-titration. Where feasible, electrolytic titration using a soluble anode was practiced (*134, 136*).

Tanabe and Hasegawa (*175*) studied the estimation of free acid in iron, chromium, and aluminum salt solutions.

The titration of boric acid with polyhydroxy compounds added has been studied anew by Tanabe and Hidaka (*176*), Carrero and Ramallo (*34*), and Blumenthal and Fall (*24*). The last research was in connection with the analysis of nickel boride; mannitol was added.

Roe and Mitchell (*152*) estimate carbonyl compounds by the differential pH change caused by adding hydroxylamine hydrochloride. Similar studies by the titration method have been made by de Miranda and Lemmens (*124*) and Barker and Perry (*11*).

Baker *et al.* (*9*) found eight replaceable hydrogen atoms per molecule of dodecamolybdoceric(IV) acid. The titration behavior of the following acids or mixtures has been studied: quinaldinic acid (*195*), orthophosphoric acid (*57*), barbituric acid in mixed purified purine bases (*87*), sodium salts of desoxyribonucleic acids (*111*), thiocarbamide and phenylthiocarbamide (*85*), azo dyes from aminonaphthol or its derivatives (*142*), polydicarboxylic acid, maleic acid, and styrene co-polymers (*70*), and serum constituents (*7*).

Tendeloo (*180*) has studied adsorption by titration of the three isomeric hydroxybenzoic acids and maleic and fumaric acids before and after addition to an absorbent. Van Schuylenbergh and Vervelde (*159*) determined titration curves of dialyzates from clay minerals. Mitra and Mathur (*125*) found three inflections in the titration curves of the clay minerals attapulgite (second inflection sharp) and montronite (third inflection sharp).

Electrotitration-turbidity diagrams of proteins were determined by Monnier (*126*). Acid or base was allowed to dialyze through cellophane.

A number of precipitation studies of normal or basic salts have appeared, in which pH measurement is used: arsenates of copper, lead, zinc, and cadmium by Hubicka (*90*); ferric arsenate, by Hubicki *et al.* (*92*); and ferric antimonate and ferrous thioantimonate by Hubicki and Wysocka (*93*) (cf. also *90, 91*). Pawar and Kabadi (*141*) found by pH measurement that the reaction of thorium nitrate to form gels with pyroarsenic acid, KH_2AsO_4 or K_2HAsO_4, gave a different acidity in each case.

Complex formation between cupric salts and amino acids was studied potentiometrically and polarographically by Li and Doody (*113*). Cupric nitrite complexation has been studied by Fronaeus (*66*) and copper bromide plus hydroxy acids by Nasanen and Lumme (*132*).

Nonaqueous Acid-Base Titrations. A general review of this subject was made by Riddick (*149*) last year. Keen and Fritz (*105*) reported on the microtitration of amines in various solvents.

Glacial Acetic Acid as Solvent. Markunas and Riddick (*117*) titrated choline salts of carboxylic acids in this medium. Pifer and Wollish (*143*) titrated organic bases, heterocycles containing nitrogen, and salts of quaternary bases. In the last process the addition of mercuric acetate liberated salts that could be titrated with perchloric acid made up in dioxane: $2\ N(R)_4X + Hg(OAc)_2 = 2NR_4OAc + HgX_2$, where X is Cl, Br, or I. Moore *et al.* (*127*) determined the basic nitrogen compounds in shale oil. Pyridines could be distinguished from pyrroles. Berger (*13*) was able to titrate xanthogenates in the medium, although they are unstable in hydrogen acetate.

In water-acetone medium acids of type RNH^+ become stronger as the dielectric constant decreases, and beryllium ion becomes a stronger acid. Hydrogen chloride remains strong as long as D is greater than 24. The ion product of water changes little from D 80 to 47, according to Bertin (*15*).

Freeman (*62*) titrated Schiff bases in acetic acid with perchloric acid in acetic acid, or in acetonitrile with perchloric acid in *p*-dioxane medium. The standard solutions were $0.1N$. According to Fritz (*64*), better differential titrations of amines are possible in acetonitrile than in acetic acid or water.

Fritz and Lisicki (*65*) use 0.1 to $0.2N$ sodium methoxide for titration of carboxylic acids in 3 to 1 benzene-methanol mixtures.

Tomicek and Heyrovský (*184*) found that antimony or tellurium served well as indicator electrode and platinum-palladium black as reference in glacial acetic acid.

Pifer, Wollish, and Schmall (*144*) found alcohol–*p*-dioxane mixtures a good medium for titrations.

Mixtures of acids may be titrated in dimethylformamide as solvent with the differential platinum-electrode system and chloranil-dihydrochloranil as the indicating reagent. Phthalic acid admixed with monomethyl phthalate gave three inflections. Various mixtures of oleic acid, phthalic acid, and methyl phthalate were titrated (*108*).

According to Shkodin *et al.* (*161*), anhydrous formic acid is a suitable medium in which to titrate weak organic bases.

Tomicek and coworkers (*186*) have investigated both acid-base redox and precipitation reactions in glacial acetic acid.

Katz and Glenn (*104*) applied titration by sodium aminoethoxide in ethylenediamine medium to estimation of phenols in coal hydrogenation oils. Gran and Althin (*81*) used a calomel electrode charged with ethylenediamine saturated with calomel and with lithium chloride added for reference in this medium.

PRECIPITATION AND COMPLEX FORMATION

Processes Involving Silver and Halides or Other Anions. Blaedel *et al.* (*23*) have used the concentration cell method of Furmand and Low (*68*) for the estimation of traces of chloride in solutions of high ionic strength. Spicer and Strickland (*167*) also used the concentration cell principle for chloride. Microgram quantities of chloride were collected on silver iodide and the silver and iodine were removed chemically. Silver may be determined in the presence of lead, bismuth, copper, cadmium, zinc, arsenic, antimony, and iron by titration with iodide after addition of the disodium salt of ethylenediaminetetraacetic acid and neutralization, according to Dolezal *et al.* (*47*). Mercuric ion interferes. Applications of the chloride titration with silver have been reported for biological fluids by Sanderson (*155*) and for agricultural, water, and biochemical uses by Furutami (*69*). The Pinkhof electrode system was used in the latter applications. A silver rod in a suspension of hydrogen-silver cation exchange resin was used in chloride titrations by Goodall and Mellor (*79*). Kolthoff and Kurode (*110*) found that titration to the equivalence potential at controlled ionic strength was excellent for traces of chlorides.

Schulek and Punger (*157, 158*) used a hydrogen indicator electrode in the titration of iodide with silver, with *p*-ethoxychrysoidine added. The titration of mixtures of halides or individual halides has been reinvestigated by Sierra and Carpena (*162–164*). Wade has studied the titration of bromide in the range 0.1 to 1.5 mg. (*190*).

Ricci (*148*) has given a detailed theoretical treatment of the titration of cyanide with silver.

Sack (*153*) has considered titrations of sulfate, sulfite, thiosulfate, sulfide, polysulfide, hydroxide, and carbonate. Sulfides and polysulfides were estimated by silver titration. Mixtures of sulfite, thiosulfate, and sulfide may be analyzed, according to Muller (*130*) by using iodometric methods for the former and silver for sulfide.

Mixtures of bromides and thiocyanates give two end points in 80 to 90% acetone solution, according to Léon (*112*).

The titration of fluoride with lead has been reinvestigated by Cropper (*43*) using the ferrous-ferric redox response at a platinum electrode for indication.

Achiwa (*2, 3*) found that the titration of lead with ferrocyanide gave indirect physiological indications and a sudden increase in potential was proportional to the amount of hydrolyzed protein in solutions.

Taryan *et al.* (*178*) have investigated the titration of lead with oxalate, pyrophosphate, and phosphate and also of aluminum with fluoride (*179*).

Birr (*19*) has studied methods for estimating ferrocyanide, ferricyanide, and halogens in their mixtures by a combination of silver titrations and redox methods, for application to photographic bleach solutions.

Swinehart (*171*) has applied the dead-stop technique to the zinc-ferrocyanide precipitation and to the stannous chloride iodine titration. Polyak (*145*) determines zinc in presence of aluminum, complexed with oxalate, by ferrocyanide titration.

Aldose end groups are allowed to react with excess of cyanide, which may be titrated back with mercuric nitrate, according to Yundt (*197*).

Hershenson *et al.* (*88*) have studied lead complexes by potentiometric, polarographic, and spectrophotometric methods. The lead amalgam electrode has been advocated by Dutta and Ghosh (*52*) for estimations of lead, barium, or sulfate.

Teodorovich (*181*) found an intermediate jump in potential in the titration of aluminum solutions with sodium fluoride, which is attributed to formation of AlF_2Cl or the AlF_2^+ ion.

Hazel *et al.* (*86*) have studied the precipitation of zinc in nitrate chloride and sulfate solutions with sodium hydroxide and with sodium silicate.

Okac and Tethal (*139*) used the Kirk procedure with chloroplatinic acid for the estimation of potassium.

Bordoni (*25*) used a platinum-mercury galvanometric system in titration of chloride, sulfide, or copper. No battery or potentiometer is needed.

In glacial acetic acid lithium bromide or lithium chloride may be titrated with mercuric, lead, or thallous acetate, according to Tomicek and Zukriegelova (*188*) (cf. *187*).

OXIDATION-REDUCTION TITRATIONS

Permanganate Methods. Issa and Awad (*95*) add excess of permanganate or bichromate in alkaline medium to oxidize tellurium(IV), followed by acidification and back-titration with oxalic acid or ferrous sulfate. Bertorelle and Giuffre (*17*) determined thallium(I) by titration at 40° C. in hydrochloric acid medium. Bezdek and Okac (*18*) have investigated the determination of titanium in presence of iron. Steele and Hall (*168*) determine titanium and vanadium after removal of iron and other elements to a mercury cathode by titration of the reduced solutions, allowing them to flow into ferric iron from a reductor for the sum, and by selective reduction to vanadium(IV) for vanadium alone.

Oelsen *et al.* (*156*) describes electrolytic titration for acids, and oxidants such as manganese(VII), chromium(VI), or vanadium (V).

Ceric Titrations. Takahashi *et al.* (*173*) used oxidation by excess of standard ceric solution followed by back-titration with ferrous sulfate for determination of polyhydric alcohols or alginic acid. Wells (*194*) titrated micro amounts of iron (0.27 to 0.5 mg.) with $0.005N$ nitratocerate solution after reduction in a silver reductor.

Bichromate Processes. Collier and Fricker (*40*) used a modified dead-stop method for titration of ferrous ion with bichromate in approximately normal solutions. Gokhale (*78*) allowed cuprous chloride to react with ferric alum with air excluded and titrated the ferrous ion with bichromate.

Oxides of Chromium and Manganese. Jatkar and Mainkar (*96*) report a series of intermediate oxides formed by reaction of manganese(II) with permanganate in acid and alkaline solutions, and a similar series for chromium (*97*).

Periodate. Singh *et al.* (*166*) report determinations of mercurous, stannous, arsenious, and antimonous compounds and of hydrazine and thiocyanate by reaction with potassium periodate. Mazor and Erdey (*120*) determine bivalent vanadium with periodate. Zinc is reported to be less effective than cadmium in reducing the vanadium. They report reduction of periodate to iodide in the process vanadium(II) → vanadium(III).

Bromate Processes. The direct estimation of furfural by bromate titration in presence of bromide and molybdate catalyst has been described by Domansky (*48*). Britton and Britton (*27*) have studied the titration of bromate ion by iodide ion.

Vanadate as Oxidant. Rius and Diaz-Flores (*151*) titrate titanium(III) or molybdenum(III) with vanadate which is reduced to vanadium(III). By differential processes involving titrations with vanadate or with ferric solution mixtures of titanium, molybdenum, and vanadium can be analyzed.

Hypochlorite. The indirect determination of bivalent metals that form double ammonium salts is possible by oxidation of the ammonia derived from the salt with hypochlorite or with hypobromite, according to Simon *et al.* (*165*).

Bromine. Kiess (*106*) investigated the dead-stop method in the titration of iodide with bromine.

Iodate Methods. McBride *et al.* (*115*) applied potentiometric titration to iodine chloride or iodine end points in the titration of hydrazine or of its organic derivatives (*116*). A similar study was reported earlier by Miller and Furman (*123*) on one or two derivatives. Britton *et al.* (*29*) investigated the titration of iodic acid with iodide.

Mixtures of Copper and Oxidants. Nievas and Berges (*133*) studied mixtures of copper and iodate, bromate, or permanganate. Iodate is determined after complexing copper with citrate and adding iodide. Similar methods are applied to the other oxidants.

Ferricyanide. Adams *et al.* (*4*) used the derivative method (*146*) for the titration of glucose. Matsuno and Sano (*119*) used both the ferricyanide and the copper methods for the estimation of glucose.

Ferrous Solutions. The titration of chromate and vanadate after persulfate oxidation and reduction of permanganate by oxalate or for vanadium alone by nitrite followed by urea has been reinvestigated by Enghag (*55*). Nitrous acid reacts with bichromate and oxalate should be used to destroy permanganate if it is present.

Iodine and Iodide Methods. The use of the Karl Fischer method for moisture in food products has been studied by Frediani *et al.* (*61*). Titration of bisulfites with or without formaldehyde added in buffered media is described by Bertorelle and Giuffre (*16*). Knowles and Lowden (*109*) found the amperometric method more satisfactory than the dead-stop or the derivative method for very dilute iodine-thiosulfate titrations. Tanner and Rentschler (*177*) found the dead-stop method suitable for estimation of sulfites with iodine in colored fluids. Swinehart (*171*) found the dead-stop method satisfactory for titration of stannous chloride by iodine. Foster and Smith (*58*) used a differential null procedure for titration of the branched starch fraction with iodine. A similar half cell with potassium chloride and potassium iodide present was titrated to restore balance after iodine was added to the starch. The process is a type of concentration cell method. The dead-stop procedure was found by Abrahamson and Linschitz (*1*) to be useful in the determination of organic peroxides.

After tellurium(IV) is treated with excess of thiosulfate, the excess thiosulfate is determined with standard iodine according to Johnson and Frederickson (*98*). Selenium is determined along with tellurium in the process.

Nitrous Acid and Nitrite Processes. The reaction of nitrous acid with iodide has been studied potentiometrically by Britton and Britton (*28*). The titration of primary amines has been investigated by several workers: Matrka (*118*) investigated amines and dihydroxyphenols, etc., with platinum-calomel and with bimetallic systems. Ferrero and Brehain (*56*) as well as Stone and Scholten have applied the dead-stop method to the diazotization reaction (*170*). Saeki (*154*) has also studied the potentiometric method in this application.

Mercurous Nitrate as Reductant. Belcher and West (*12*) have investigated extensively the reducing action of mercurous solutions in presence of thiocyanate. Many of the studies are nonpotentiometric. The determination of iron in ferric thiocyanate in presence of nonreducible coloring material is described (*12*). Hubicki *et al.* (*91*) found that nitrate, sulfate, selenate, and chloride did not interfere in the potentiometric titration of selenious acid with mercurous nitrate. Burriel and Lucena Conde (*30*) have also reported on the titration of ferric thiocyanate by mercurous nitrate.

Chromous Solutions. Rienacker and Jerschkewitz (*150*) used chromous solution to titrate copper in presence of iron. Wakkad and Rize (*191*) found that tungsten could be titrated in presence of phosphate with 5 moles of citric acid per mole of tungsten and in 36% hydrochloric acid. Muraki (*131*) has reinvestigated the preparation and standardization of chromous salts. Copper was the standard substance. Chlebovský and Brháček (*39*) determined copper, tin, and antimony with chromous chloride in strongly acidic medium with much magnesium chloride present. Busev (*32*) restudied the titration of bismuth with chromous solution. Burriel and Suarez-Acosta (*31*) studied chromous and stannous titrations of molybdenum in steels. Manganese, chromium, and vanadium interfere.

NONAQUEOUS MEDIA

Lithium Aluminum Amide. Higuchi *et al.* (*89*) have reported on the titration of very weak bases with this reagent.

Glacial Acetic Acid. Tomicek and associates have made extensive studies of redox reactions in this medium. Tomicek and Heyrovský (*185*) studied the oxidation of arsenic(III), antimony(III), mercury(I), pyrocatechol, resorcinol, hydroquinone, and diphenylamine with bromine. Chromic anhydride was found unsuitable for arsenic but useful for titrating antimony, iron, titanium, and the organic reductants. Sodium permanganate was useful for titanium, iron pyrocatechol, or hydroquinone. Reductions of ferric salts or chloranil with titanous chloride were studied. Bromine was used by Tomicek and Valcha (*187*) for titration of a number of organic compounds. Lead tetraacetate was also useful for the oxidation of ascorbic acid, hydroquinone, and pyrocatechol. Tomicek and Heyrovský (*184*) used bromine to titrate sulfamides. Tomicek *et al.* (*182*) studied the titration of unsaturated substances with bromine.

Luk'yanits and Nekrasov (*114*) used the platinum-calomel electrode system in the titration of organic sulfides with potassium iodate in 90% glacial acetic acid.

Liquid Ammonia. Watt *et al.* (*192*) studied the titration of halides of aluminum, gallium, indium, and thallium with potassium in liquid ammonia. Gallium and indium show three electron changes, but thallium (O) reacts with thallium chloride to show intermediate formation of thallium(I). Watt and Otto (*193*) used platinum electrodes, one in a capillary with small portion of the solution surrounding it, for the titration of polysulfides with potassium in liquid ammonia.

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Chromatography

And Analogous Differential Migration Methods

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THE early reviews in this series were devoted solely to the subject of chromatography. Subsequently chromatographic techniques were recognized as prototypes of numerous analytical methods based upon the phenomenon of differential migration (*165, 171*). Consequently, the scope of this review has been extended to include a number of these related, widely applicable, differential migration techniques.

In the 2 years following the last review in this series (*165*), there has been an enormous acceleration in the development, the improvement, and the application of differential migration methods of analysis. In many productive research laboratories, several of these methods now serve as adaptable tools for exploration, for control, and for corroboration (*34, 66, 73, 120, 128, 170*). This increase in the number and applications of these basic analytical tools and a concomitant multiplication of the workers versed in their use have stimulated progress in all aspects of science concerned with chemical substances and their reactions. The resultant expansion of knowledge has been so rapid, so great, and so diverse that it cannot be cited here. Even the specialized literature pertaining to the development of the tools themselves can scarcely be summarized in the space allotted to this review.

The examination and correlation of current reports have been complicated tremendously by the description of many minor modifications of earlier methods. Moreover, many of these reports do not include references to the earlier investigations. A note on the separation of chloroplast pigments by paper chromatography (*11*), for example, gives no reference to the early reports on the formation of chromatograms with these pigments, observations which formed the foundation of columnar and paper chromatography (*163, 164*).

For economy, the citations in this review have been restricted to books (*2, 6, 19, 26, 42, 49, 95, 98, 130, 141, 156*), surveys (*10, 16, 27, 31, 32, 35, 41, 64, 74, 82, 90, 91, 102, 105–107, 109, 118, 127, 129, 131, 158, 160, 164, 165, 171, 174, 182, 184*), bibliographies (*69, 104, 123*), and current reports on basic procedures. This selected material should provide a key to the rapidly expanding literature. Many of the modifications and applications of the techniques can be found only by perusal of the literature of specialized fields.

DIFFERENTIAL MIGRATION ANALYSIS

Basic Conditions. For the examination and correlation of various separatory techniques, the concepts of differential migration analysis have now been restudied and extended. In all these methods of analysis, the migration itself is produced by the application of one or more driving forces, and it is usually opposed by resistive forces. For effective separations, either or both the driving force and the resistive forces must act selectively upon the migrating substances. The effects of a nonselective driving force (gravity) acting upon two different kinds of particles with and without a selective resistive force (viscosity) are illustrated by Figure 1.

In differential migration analysis, the migration conditions must be selected so that the components of each mixture migrate at different rates. The migration rates are a property of the migration system. They depend upon the properties of the migrating substances, upon the properties of the migration medium, and upon the nature and intensity of the driving force.

The degree of resolution depends upon the dimensions of the initial zone of the mixture, upon the arrangement of this zone in the medium, and often upon the concentration or the amount of the mixture. It also depends upon the differences among the migration rates of the constituents and upon the distance of the migration.

Substances separated by differential migration are located, compared, identified, and estimated by their physical, nuclear, chemical, or biological properties. Dependent upon the circumstances, the components of mixtures may be located in the medium either during the migration or after the migration. They may also be examined after removal from the respective parts of the medium.

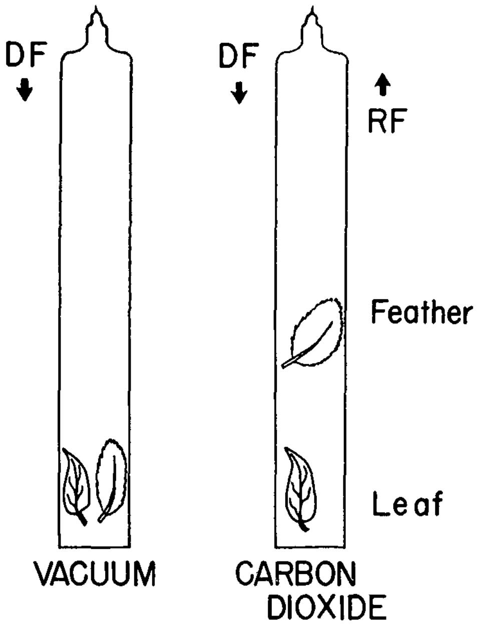

Figure 1. Uniform Migration (*left*) and Differential Migration (*right*)

Migration with a nonselective driving force (*DF*, gravity) unopposed by a resistive force (*left*), and differential migration with a nonselective driving force opposed by a selective resistive force (*RF*, viscosity of gas) (*right*)

Because separations are frequently most effective when the concentration or amount of the mixture is small, and because minor constituents must be located, many novel and sensitive detection and assay methods have been devised. These detection methods are without influence upon the differential migrations. They depend upon various properties of the separated substances, as, for example, refractive index, optical interference, fluorescence, spectral emission, spectral absorption (*28*), dielectric properties with high frequency current (*67, 117*), radioactivity (*10, 21, 144, 175*), nuclear activation (*94, 112, 175*), formation of colored products by staining procedures (*88, 89, 133*) and by chemical reactions (*15, 52, 73, 100, 101*), bleaching of colored reagents (*100*), reactions with hormones or enzymes (*170*), the inhibition and the stimulation of the growth of living organisms (the so-called bioautographic methods) (*29, 153*), and many others (*19, 95, 130*).

Materials to Be Separated. With respect to their physical condition, the materials to be examined by differential migration may be gases, liquids (including solutions), solids, and various combinations of these. With respect to size, these materials may be atomic particles, ions, isotopes, molecules, colloids, and microscopic and macroscopic bodies. They may be natural or synthetic substances of organic or inorganic nature, and they may even be living organisms.

The components of the mixture should not be bound irreversibly with one another. Ionized or dissociable substances are usually separated into the several ionic or dissociated species.

Migration Media. Migration media may be vacua, gases, liquids, or solids. With the same driving force, substances migrate fastest in vacua, slower in gases, and much slower in liquids, in gels, and in hydrated resins (*92, 100, 159, 172*). The migration rate in most solids is so slow that these materials are not widely employed as migration media (*8, 9*).

Zones of gases and liquids have been stabilized in porous media (*19, 21, 26, 95*), including permeable membranes (*45*). Liquids have also been stabilized in tubes, capillaries (*4, 12, 167*), annular spaces (*79*), gels (*88, 89, 125*), porous rods (*18*), and fibrous media such as paper, chamois, and felt (*19, 26, 95, 100*). They have likewise been stabilized in tubes containing many close baffles (*36*) and in packed centrifuge beds (*116*).

Driving Forces. Driving forces are any combination of conditions that cause particles to migrate. These forces may be classified from many points of view. With respect to their effect upon the distribution of the particles in the migration medium, driving forces fall into two principal groups—those that cause all the particles of each species to migrate, and those that cause the particles of each species to redistribute themselves in the migration system.

Forces that can cause all the particles of each species to migrate (usually unidirectionally) and the kinds of particles with which they are effective are:

Mechanical forces	Microscopic to macroscopic bodies
Gravity	Microscopic to macroscopic bodies
Centrifugal forces	Colloids to macroscopic bodies
Ultracentrifugal forces	Molecules to microscopic bodies
Magnetic forces	Magnetic particles, moving ions, particles with a dielectric different from that of the surrounding medium and exposed to an electrical field (*83*)
Electrical potential	Ions, colloids
Oscillating electromagnetic fields	Ions
Flow of liquids	Ions, molecules, colloids, microscopic and macroscopic bodies
Flow of gas	Ions, molecules, colloids, and microscopic bodies

Forces that produce redistribution of particles in the migration system, and the kinds of particles with which they are effective are:

Translational energy	Ions, molecules, colloids (self-diffusion)
Chemical potential gradients	Ions, molecules, colloids (diffusion) (*34, 80, 150, 151*)
Thermal gradients	Ions, molecules (thermal diffusion) (*12, 37, 79, 81, 86, 147, 148, 167*), (thermal osmosis) (*45*), (distillation) (*4, 87, 137*)

Driving forces differ with respect to their selective action upon the migrating particles. Some are nonselective; others are highly selective. The selectivity, however, depends upon the properties of the particles themselves and upon the properties of the migration system. When two or more driving forces are utilized, the combined effect is the vector resultant force.

Resistive Forces. Resistive forces are the conditions in the migration medium that resist the migration of the particles. These conditions include viscosity, density, density gradients, hydrostatic gradients, sorption, and permeability of the medium, including the permeability of molecular and mechanical barriers.

The sorption of solutes or gases by the migration medium is one of the most selective and adaptable resistive forces. This sorption, which is the selective, resistive force in chromatography, depends upon a variety of distribution phenomena in which the sorbed substances are distributed dynamically between a fixed nonmobile phase and a mobile gaseous or liquid phase.

It serves for the separation of all kinds of chemical substances, but it is not very effective with isotopes or with optically active, enantiomorphic substances (*14, 22, 99, 140*).

Barriers also provide a selective and adaptable resistive force. Barrier membranes permit the selective filtration of polysaccharides (*120*). They facilitate the separation of solutes from colloids by dialysis and by electrodialysis (*66, 134, 168, 182*). Screens and the like provide the selective barriers for many mechanical separations. Porous barriers provide the stabilizing medium for the fractionation of isotopes by gaseous diffusion.

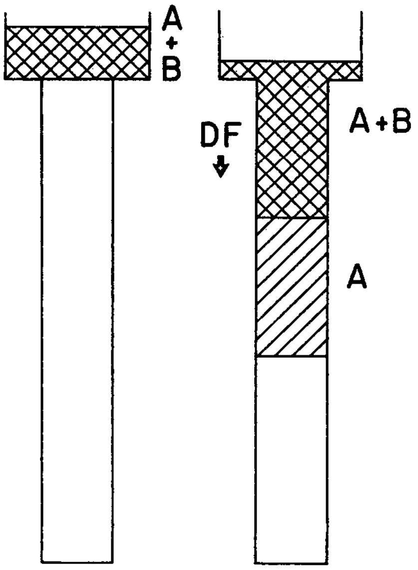

Figure 2. Differential Migration from a Reservoir

Start (*left*) and partial separation of leading zone (*right*)

Many resistive forces act uniformly, so that each kind of particle migrates through the medium at a constant rate. A few resistive forces, particularly density and hydrostatic gradients, provide increasing resistance to migration, so that the migrating particles come to a standstill when the resistive force equals the driving force. An example is the sedimentation of virus particles in a medium with a suitable density gradient (*23, 161*). An analogous effect is the behavior of the Cartesian diver in a medium with a density gradient (*56*).

Arrangement of Zone of Mixture. The arrangement of the initial zone of a mixture determines, in large measure, the separations that may be effected by particular combinations of driving and resistive forces. With a single driving force, there are four principal arrangements for the migration: uniform distribution of the particles in the migration system followed by differential redistribution, differential migration from a reservoir of the mixture, migration from a zone so wide that the mixture is but partially resolved in the medium, and migration from a zone so narrow that all or most of the components of the mixture are separated in the migration medium. With two driving forces acting transversely to each other, the particles may be distributed throughout the medium, or they may form a wide initial zone, a narrow spot, a wide stream, or a narrow stream.

Differential Redistribution in the Migration System. In a closed or limited migration system, and with a driving force that produces redistribution of the particles, the migration reaches a steady state in which overlapping zones or concentration gradients are established for each kind of particle. The degree of separation depends upon the dimensions of the system, the location in the system, the properties of the components, and the nature of the driving force.

This differential distribution in a closed system is the basis for the thermal diffusion of gases, and for the thermal osmosis of gases through a membrane (*45*). In closed systems, differential distribution in one direction is frequently combined with migration in a transverse direction. Thermal diffusion transverse to gravity is especially effective for the fractionation of isotopic gases (*12, 36, 37, 81, 86, 87, 147, 148*), and it has been utilized for the fractionation of liquids such as tall oil (*79*). This combination of forces resembles that in the distillation column (*87*), also adapted to the separation of isotopes (*4*), but here the separation of the vapors of the components is enhanced by the intervening zones of the condensed refluxing phase (*4, 12, 87, 137*). An analogous effect is obtained in the thermal diffusion column by the addition of "Hilfsgase," gases that form zones between those to be separated (*37, 147, 148*).

In solutions, electrical migration transverse to gravity provides electrical migration-convection methods (ionophoresis-convection; electrophoresis-convection) that are widely adaptable to the separation of various ions and proteins (*134, 168, 170*). These separations may be made more effective with suitable membranes as barriers (*168*).

Migration From a Reservoir. Analysis by differential migration from a reservoir is illustrated schematically by Figure 2. This arrangement is utilized with both kinds of driving forces, those that produce migration of all the particles and those that produce redistribution of the particles. It provides but a partial resolution of the mixture. Only a portion of the fastest migrating constituent is separated from the others. The proportions of the constituents in the overlapping, migrating zones are altered, however, so that repeated recovery and remigration produce a gradual fractionation of the mixture.

With this migration from a reservoir, the number of the advancing boundaries provides an indication of the number of the components in the mixture. Under standardized conditions, the rate of the migration serves as a basis for identification and estimation of the migrating substances.

The migration may be linear, as illustrated in Figure 2. It may also be radial (*116, 174*) as from a narrow source into a sheet or flat mass of the medium; or it may be segmental as from a point source into a three-dimensional mass of the medium in the form of a sphere, a solid angle, or a cone (see discussion on paper chromatography).

This migration from a reservoir is employed for the differential diffusion of gases and of solutes (*80, 96, 150*), for the electrical

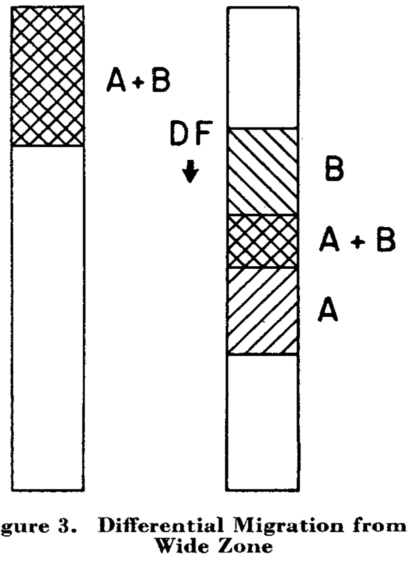

Figure 3. Differential Migration from a Wide Zone

Start (*left*) and partial separation of leading and trailing zone (*right*)

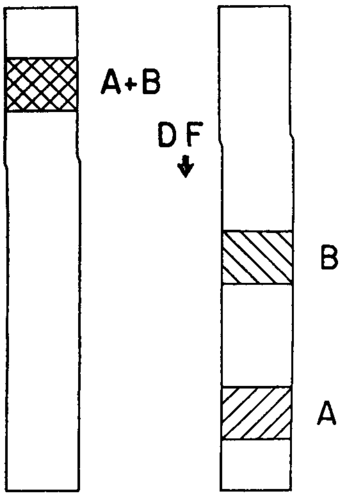

Figure 4. Differential Migration from a Narrow Zone

Start (*left*) and resolution of the mixture (*right*)

moving boundary method, for decolorization of solution with sorption columns, for fractional extraction, and for some spot tests in paper. It is the basic arrangement for breakthrough analysis (*64*, *80*, *151*), for frontal analysis (*19*, *26*, *95*), and for the capillary adsorption analysis in paper strips so widely applied by Goppelsroeder (*164*). It is analogous to the common arrangement for sedimentation and centrifugation procedures in which the trailing boundaries of the zones reveal the composition of the mixture (*23*, *34*, *63*).

The absorption and the excretion of chemical substances by living organisms are analogous to the differential migration of solutes from a reservoir. Indeed, the selective or differential permeability of the kidney is duplicated by the membranes of the "artificial kidney" (*182*). These selective processes of living organisms often yield a partial separation of isotopes (*3*, *10*, *47*).

Differential migration from a reservoir coupled with a transverse migration permits the fractionation of large quantities of mixtures. As a rule, the separations are incomplete and are similar to those illustrated by Figure 2. An example is the selective sorption of solutes at a gas-liquid interface followed by their removal as foam (*17*, *128*). Another example is the diffusion of solutes through a membrane system with transverse flow of solvent. In practice, this arrangement for separations is usually more effective when operated as a countercurrent process and examples are reported in the section on migration from a wide stream.

Migration from a Wide Zone. Differential migration from a wide initial zone, as illustrated in Figure 3, is effective with those driving forces that cause all the particles of each species to migrate. With driving forces that produce redistribution of the particles, the migration from a wide zone yields separations resembling those of Figure 2.

Migration from a wide zone provides but partial resolution of the mixture, only a portion of the fastest and slowest migrating substances being separated. This migration arrangement may be utilized in much the same way as migration from a reservoir. Both the trailing boundaries and the leading boundaries provide information about the number, the nature, and the proportions of the components.

Differential migration from a wide zone is utilized in sedimentation analysis (*34*, *63*, *161*), with sorption columns (*9*, *181*), and with strips or sheets of sorptive paper. It is the basic arrangement for certain modifications of the electrical moving boundary method (*39*) and for the related differential electrophoresis of proteins (*2*, *12*, *88*, *89*, *106*, *107*).

Migration from a Narrow Zone. Differential migration from a narrow initial zone of the mixture provides the most effective arrangement for the resolution of mixtures. With this arrangement, modifications of which are illustrated by Figures 4 to 7, the driving force should cause all the particles of each species to migrate. Procedures based upon this arrangement represent batch processes for the resolution of mixtures. They make possible the complete resolution of multicomponent mixtures of solutes, of vapors, and of gases. They are, therefore, of the greatest usefulness, particularly to chemists whose methods for the determination of physical and chemical properties depend upon the resolution of mixtures and upon the isolation of the components in a state of high purity.

Differential migration from a narrow zone produced with a single driving force is illustrated schematically in Figure 4. The migration may be linear as illustrated, radial, or segmental (see section on paper chromatography). Dependent upon their properties, the particles may migrate in one direction only (Figure 4) or they may migrate in opposite directions, as with positive and negative ions during electrolysis (Figure 5) (*143*, *144*, *162*).

This linear migration from a narrow zone is a critical feature of some of the most important differential migration methods as, for example, chromatography, electrochromatography, sedimentation, and centrifugation. It is also a critical feature of the time-of-flight mass spectrometer (*13*, *55*, *57*).

In this instrument, ions from a narrow source are accelerated intermittently by a pulsating electrical field in vacuum, so that only those of a particular mass and velocity pass through a barrier consisting of another synchronous, pulsating, electrical field (*55*).

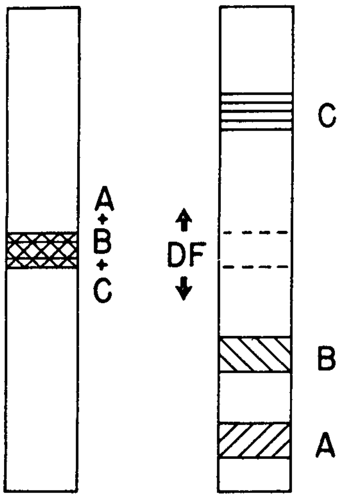

Figure 5. Differential Migration from a Narrow Zone

Components migrating linearly and in opposite directions as in electrochromatography. Start (*left*) and resolution of the mixture (*right*)

This differential migration from a narrow zone may also be produced with two driving forces in opposition, or it may be caused by two unique driving forces applied transversely. These two transverse forces may be applied intermittently or in succession. They may also be applied simultaneously.

Two opposed driving forces, flow of solution and electrical migration, have been utilized in the separation of ions. With moist paper as the medium for differential electrical migration, flow of the solution opposed to the ionic migration may be produced by electro-osmosis (*105*, *106*), by hydrostatic pressure, or by evaporation from the paper (electrorheophoresis) (*108*). Gravity opposed by density gradients provides the basis of various sink-and-float separations of microscopic particles and macroscopic bodies (*161*). It is also the basis of various ore flotation processes.

With Cartesian divers, this combination of forces provides a convenient analytical method for following changes in the density of various reaction systems (*23*).

Migration from a narrow zone with two unique driving forces applied transversely and in succession is illustrated by Figure 6. This is the basic procedure of the two-way paper chromatography with flow of two different solvents in succession (*44*, *101*, *164*). It is also the basic procedure for two-way and three-way electrochromatography with electrical migration in different solvents (*46*, *162*), and of combinations of flow of solvent with electrical migration (*40*, *133*). As indicated by Figures 6 and 7, the position of the separated substances relative to the paper depends upon the direction in which each force is applied (*44*). The degree of resolution does not (*101*). The paths followed by the solutes do depend, however, upon the sequence in which the forces are applied. In reports concerning the sequences of substances separated by forces applied transversely, the direction of each force should be specified. If there are anomalous trailing effects (*40*, *108*, *154*) or if the solvents alter the medium (*124*), the sequence of the application of the forces should also be reported.

Migration from a narrow zone produced by two forces applied transversely and simultaneously is illustrated by Figure 8. Here the net result is the same as that obtained by application of the forces in succession. But the paths followed by the solutes are different from those indicated by Figures 6 and 7. A patent pertaining to the separation of mixtures in a narrow spot by the simultaneous flow of solvent transverse to electrical potential indicates that "the novel combined action . . . accomplishes results not obtainable by chromatographic or electrostatic separation severally" (*68*). From the views set forth here, the separations obtained by the simultaneous application of the forces may also be obtained by application of the forces in succession.

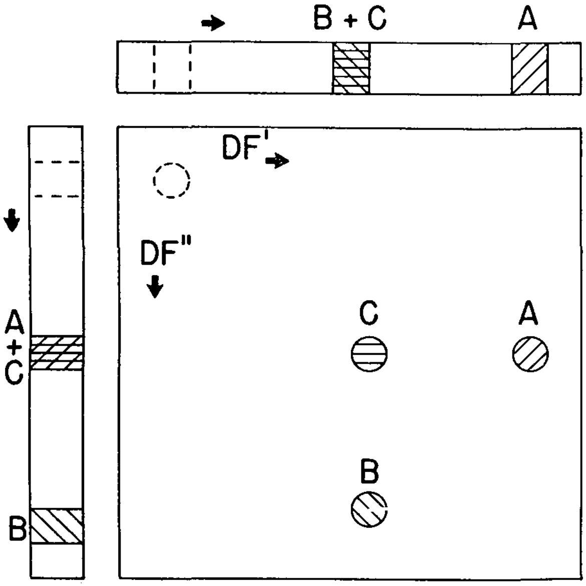

Figure 6. Differential Migration from a Narrow Zone

Two unique forces applied transversely and in succession. Force *DF'* (*top*) and force *DF''* (*left*) yield but partial separation. Forces applied transversely and in succession (*center*) produce complete, two-way separation.

In these differential migration procedures, the narrow zones often become diffuse and enlarge as the migration proceeds. This effect may be attributed to diffusion (*62*, *96*) and to the heterogeneity of the migration medium. With similar solutes, such as rare earths, or isotopes, or proteins, the rate of enlargement of the zones often exceeds the difference between the rates of migration, so that the zones overlap and the components are not separated completely from one another (*44*, *143*, *154*, *162*).

Differential migration from a narrow zone is the basis of the batchwise, countercurrent, partition procedure introduced by Craig (*41*, *127*, cf. *38*, *103*, *114*, *122*). In this method, mechanical force produces intermittent counterflow of the two immiscible liquids. As in chromatography, differential distribution of the solutes between the two liquid phases is the selective factor. Because the migration is carried out as a series of batch distributions, the separations per unit length of the system are not so effective as those performed with one of the liquids fixed in a partition column.

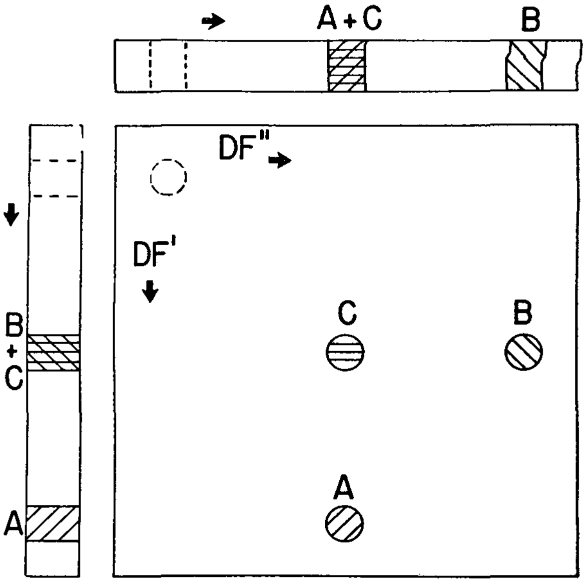

Figure 7. Differential Migration from a Narrow Zone

Two unique forces applied transversely and in succession, as in Figure 6, but with the direction of the forces interchanged. Compared to Figure 6, position of the separated zones relative to the medium is changed, but degree of separation is not.

Migration from a Wide Stream. When a wide stream of a mixture is exposed to two transverse forces, arranged as in Figure 9, a partial resolution occurs at opposite sides of the stream. With this arrangement the fractionation process may be operated continuously.

An analogous, continuous, partial fractionation is achieved by many countercurrent procedures (*80*, *151*) in which the components of the mixture migrate transversely and differentially from one stream to another. With flow of two gas streams as in "free double diffusion" (*150*), the streams are separated by a porous barrier. With solutions, the streams may be separated by ion exchange membranes (*158*) or by semipermeable membranes. The intervening, porous, migration barrier may even be a complex differential migration unit, as with electromigration-convection operated continuously.

Migration from a Narrow Stream. With two unique, transverse forces applied to a narrow stream of the mixture, each component follows a separate path through the migration medium and emerges at a different position, as shown by Figure 9. This procedure may not only be operated continuously, but it also serves for the complete resolution of multicomponent mixtures as in continuous electrochromatography (*24*, *25*, *58*, *72*, *99*, *145*). The two forces may be applied simultaneously as in continuous electrochromatography, or in succession as in the early modifications of the mass spectrometer. They may also be applied intermittently as the electrostatic field in the cyclotron and in the ion resonance mass spectrometer (*119*, *157*).

CHROMATOGRAPHY

Evolution and Definition. The number of recent publications concerning the modifications and applications of chromatography has been phenomenal. The gradual adoption of Tswett's "chromatographische adsorptions Analyse" by chemists first led to an entry for "chromatographic" under "adsorption" in the *Chemical Abstracts* Decennial Index for 1927–36. Not until 1943 was "chromatographic adsorption" made a major entry with 38 citations. In 1950 the citations were entered under "chromatography and adsorption analysis," and in 1952 there were some 1000 citations under this heading.

Most of the recent investigations have concerned diverse applications of the chromatographic technique. Many have been devoted to modifications of the apparatus and procedure. Much has been written about the definition (*164*, *179*) and the evolution of chromatography (*51, 164, 174, 176, 178, 179*). Ten books, several bibliographies, and numerous reviews have summarized various aspects of the technique and its applications (see reviews). All this progress has been so specialized and so rapid that the analytical meaning of chromatography is just now finding its way into the encyclopedias and the dictionaries which heretofore have included only the older definition—a treatise on colors.

With respect to procedure, there is a clear distinction between the flow of solutions through sorptive systems (Figure 2) and the formation of a chromatogram with fresh solvent or wash liquid (Figure 4). Contrary to recent contentions (*51, 176, 178, 179*), the formation of a chromatogram, as reported by Tswett in 1903 and in 1906, must be regarded as the pinnacle in the evolution of the chromatographic technique (*164*). Chromatography is a unique procedure among a number of closely related techniques. It is no longer restricted to use with pigments, nor is it dependent solely upon the use of surface active adsorbents. In time the meaning of chromatography or sorptography may be extended to include all the similar methods of which chromatography is the prototype (Figure 4), or another collective name for these methods may be devised, leaving chromatography with its present meaning. The following definition, which differs from some recent proposals (*178, 179*), is based upon the principles outlined in this review. Chromatography is the study and the utilization of widely applicable, analytical procedures for the resolution of mixtures of solutes by differential migration from a narrow zone in porous media, the migration being produced by electrical potential or by flow of liquid or gas.

Subdivisions of Chromatography. From the practical viewpoint and in harmony with the definition, there are three principal subdivisions of chromatography: chromatography by flow of solvent or gas, chromatography by electrical migration, and chromatography by various combinations of flow of solvent and electrical potential. Techniques in each of these principal divisions are commonly classified with respect to the arrangement and the nature of the migration medium as with porous columns (columnar chromatography, columnar electrochromatography), with fibrous sheets, particularly paper (paper chromatography, paper electrochromatography), or with gels or fixed liquids (electrochromatography in gels). Combinations of flow of solvent with electrical potential provide the two-way method of chromatography plus electrochromatography (Figures 6 to 8) (*40, 133*) and the continuous electrochromatography (Figure 9) (*58, 145, 160*). Electrochromatography in different solvents provides the two-way and three-way electrochromatography (*46, 162*).

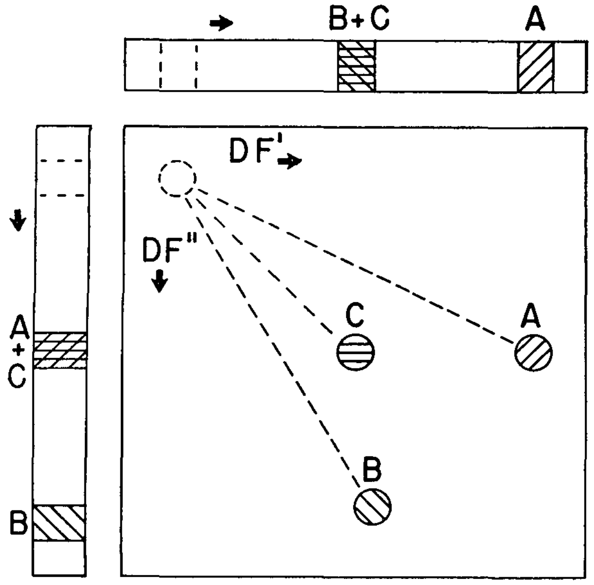

Figure 8. Differential Migration from a Narrow Zone

Two unique forces, *DF'* and *DF''* as in Figure 6, applied simultaneously or intermittently. Course of migration is vector resultant (dotted lines) of the two transverse forces. Degree of separation is comparable to that of Figure 6.

The principal groups of chromatographic methods are frequently subdivided with respect to the mechanism of the sorption process—for example, adsorption at a solid-liquid interface (adsorption chromatography), adsorption at a solid-gas interface (gas chromatography) (*9, 64, 77, 110, 111, 181, 185*), adsorption at a liquid-gas interface (foam analysis) (*17, 128*), adsorption at a liquid-liquid interface (*163*), distribution between two immiscible liquids (partition chromatography) (*74, 118, 163*), distribution between a gas and a liquid (gas-liquid partition chromatography) (*76*), distribution between a chemically reactive substance and a solution (particularly, ion exchange chromatography) (*90, 91, 118*), and partition between a liquid and a resin containing the same liquid (ion exclusion chromatography) (*177*). This classification of the chromatographic methods is subject to great variation, not only because the mechanism of the sorption process often varies with the experimental conditions, but also because several mechanisms may be effective simultaneously. Dependent upon the circumstances, paper, for example, may be an inert support, a surface active sorbent, or an ion exchange substance (*1, 30, 149, 152*). It may also fix a liquid which then serves as a partition solvent (*74, 163*) or as a surface active sorbent (*163*).

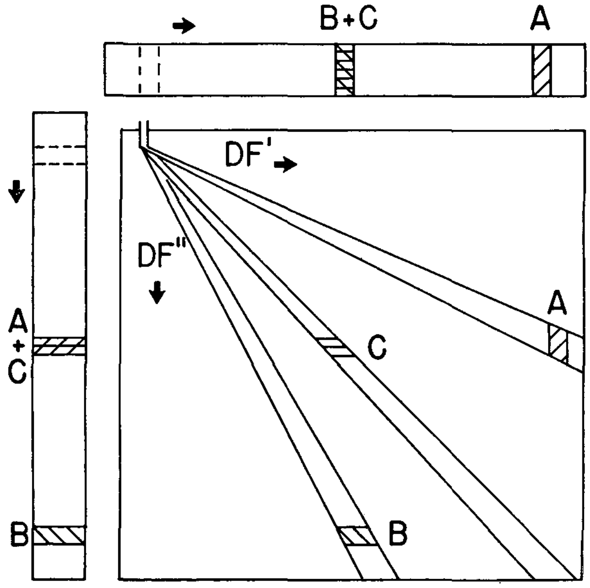

Figure 9. Differential Migration from a Narrow Stream

Two unique, transverse forces applied simultaneously or intermittently. Components of the mixture follow separate paths at different rates. Separation is continuous.

The various groups of chromatographic methods are often classified with respect to the field of application. The principal applications are analytical and preparative procedures in inorganic chemistry (*98, 130, 141, 156*), organic chemistry, biochemistry (*118*), clinical chemistry (*2, 105, 106*), and industrial chemistry (*174, 178*).

All these chromatographic methods depend upon analogous principles. The several techniques yield similar separations, and they can be modified and applied in similar ways. Their range of application varies greatly with the chemical properties of the materials to be resolved.

Reviews. The general subject of chromatography has been reviewed in a book by Lederer and Lederer (*95*). Practical techniques in many branches of chromatography have been presented by Brimley and Barrett (*26*). A review similar to the last one in this series (*165*) has been prepared by Tiselius (*171*).

The field of paper chromatography has been surveyed in three books, by Cramer (*42*), by Block, LeStrange, and Zweig (*19*), and by Balston and Talbot (*6*). The latter publication also includes results obtained with columns of powdered cellulose. Astonishingly, none of these publications have included Brown's early observations on the separation of chloroplast pigments by circular paper adsorption chromatography or Liesegang's cross capillary analysis (two-way paper chromatography) (*164*).

Electrochromatography, particularly as applied to protein separations, has been reviewed by Antweiler (*2*) and by McDonald and his coworkers (*105, 106*). Conditions requisite for the separation of inorganic ions have been presented by Sato *et al.* (*144*). Electrochemical separations in ion exchange resins have been reviewed by Spiegler (*158*).

Bibliographies of electrochromatography have been collected by McDonald (*104*) and by Henley and Schuettler (*69*). The latter bibliography contains much material relating to the applications of electrochromatography and to the detection of zone boundaries in chromatographic systems.

Comprehensive books on inorganic chromatography have been prepared by Lederer (*98*) and by Pollard and McOmie (*130*). Inorganic chromatography has been cursorily reviewed by Smith (*156*), who has placed major emphasis upon his own tests of analytical procedures. Practical identification procedures based upon flow of solutions into sorption columns (Figure 2) have been presented by Fillinger for cations of the common qualitative groups (*49*, cf. *50*).

Applications of ion exchange resins in analytical chemistry have been summarized by Samuelson (*141*). An extensive bibliography pertaining to the analytical applications of ion exchange resins has been prepared by Osborn (*123*). The electrochemical properties of resins (*158*) and of resin membranes (*180*) have also been summarized.

Many aspects of the important field of partition chromatography (*74*) are cited in the books dealing with chromatography, paper chromatography, and inorganic chromatography. Routine applications of chromatography, which number about 2000 for 1953, may be found in *Chemical Abstracts*, in various reviews including those published by Annual Reviews, Inc. (*118*), and in the literature pertaining to particular subjects and materials (*10, 53*).

Theory and Distribution Mechanism. Most theoretical treatments of chromatography are concerned with the kinetic aspects of the distribution mechanism. They relate to zone formation, zone boundaries, and zone migration (*92, 136, 138, 172, 173*).

Thus far no comprehensive theory has been proposed for estimation of the distribution of a solute between the two phases of various chromatographic systems. Solubility provides a clue to the distribution of solutes between two immiscible solvents, and "solvent theory" and the solvent properties of various liquids provide a clue to their effect on the sorption of various solutes (*71*).

The sorption of solutes on a surface active sorbent is one of the most widely applicable distribution mechanisms employed for chromatographic separations. These sorbents attract all kinds of solutes. They sorb hydrocarbons from the least polar, saturated hydrocarbon solvents, and they sorb polar solutes from polar solvents such as water. Many other distribution systems are not so widely applicable. The selective partition between immiscible solvents, so widely employed in columnar chromatography and in countercurrent extraction, is limited by the miscibility of solvents that have suitable affinities for the nonpolar solutes (*163*) or for the strongly polar solutes. Many of these partition systems are, however, finding wider application for the separation of fatty, nonpolar substances (*38, 103, 114, 122*).

From a theoretical viewpoint, each solute should form a single zone in a chromatographic system. In practice, on the contrary, alteration of the solute (*70, 154*) or variation of the sorptive system (explored with chloroplast pigments in 1950) may yield two or more zones (*20, 43, 61, 124, 154, 155*) and may affect the migration rate or the migration distance of proteins when washed with phosphate buffers (*20, 61*).

Experience has now shown that phosphate ion is not sorbed by paper (*144*). Cations are strongly sorbed. When phosphate buffer flows through paper, a pH gradient is formed. This gradient determines the location and the migration rate or R value of sorbed solutes such as proteins. This effect resembles the action of sorbed solvents and impurities upon the migration rates of chloroplast pigments.

Columnar Chromatography. Columnar chromatography continues to be widely employed with various powdered sorbents (*95, 118, 130, 156*). These sorbents include vulcanized rubber (*121*), polysaccharides such as sucrose, cellulose, and starch as well as the activated sorbents, such as activated magnesium silicate, charcoal, lime, magnesia, and alumina (*53*). They also include the ion exchange resins (*90, 126*), hydrated filter aids, powdered gels, and rods of calcium sulfate (*18*).

Columnar chromatography serves for preparative purposes and on an industrial scale (*178*) as well as on a micro scale. It is often employed as a preliminary or intermediate step in the

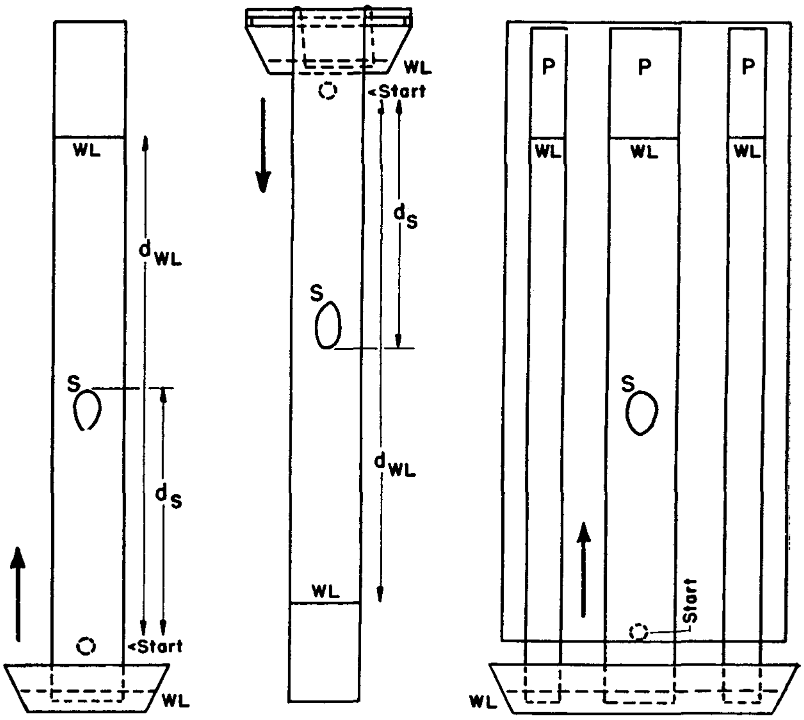

Figure 10. Arrangements for Linear Paper Chromatography

Upward linear flow (*left*) and downward flow (*center*) (performed in closed vessels). linear flow at various angles (*right*) (between glass plates)
S. Solute
WL. Wash liquid
P. Paper
d. Distance of migration
For these conditions, R_f value is designated as lin. $R_f = d_S/d_{WL}$.

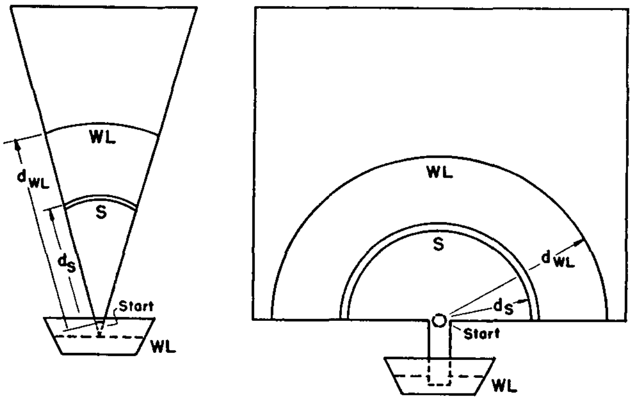

Figure 11. Arrangements for Radial (Sector or Circular) Paper Chromatography

Radial flow in a planar mass, as a narrow sector (*left*) and as a wide sector (*right*)

rad. $R_f = d_S/d_{WL}$

isolation of natural products, particularly on a large scale with fractional elution or extraction of the sorbed substances.

The location of the resolved substances in columns by the use of reagents is not so convenient as the location of substances resolved in paper (*30*). With sensitive physical, optical, and tracer methods, the separated substances may be detected as they are washed through the column.

So far as has been reported, the resolving power of columns of cellulose is comparable to that of paper (*6*). When various combinations of sorbents and solvents are employed, the resolving power and the applicability of columns are much greater than those of paper. This resolving power may be increased even further by submitting the fractions obtained from one column to further fractionation in columns of other sorbents and solvents (*53, 126*).

Paper Chromatography. Paper chromatography is a remarkably adaptable and sensitive analytical procedure (*6, 19, 42, 176, 184*). It is effective with very small quantities of mixtures of inorganic (*43, 48, 132, 166*) and organic substances. It is readily adapted to two-way (*101, 133*) and polydimensional (*44*) migrations (Figures 6 to 9). The paper may be employed as a surface active sorbent (*163*) or as an ion exchange sorbent (*1, 78, 149*). It is widely employed with a fixed solvent (*101*), as in paper partition chromatography (*74*) and in reversed phase partition chromatography (*5, 7, 28, 85, 113, 115, 163*). The paper may be altered so that it becomes chemically reactive (*48*), as an anion or a cation exchange substance (*14, 60, 78, 93*) or so that it exhibits hydrophobic rather than hydrophilic properties (*5, 85, 113, 115*).

Paper strips and sheets have usually served for linear migration (*132*). For short distances of migration, the flow of the solution may be upward, downward, or at various angles. For long distances of migration, the flow should be downward (Figure 10).

With radial migration as introduced by Brown in 1939 (*164*), the flow is through the sector of a circle (Figure 11). This technique, which is frequently called sector, radial, ring, or circular paper chromatography (*15, 54, 139, 169*), has been modified in many ways, as by the addition of wash liquid through wicks, tabs, capillaries, and dropping funnels (*15, 54, 169*). As with paper strips, it serves for the comparison of substances which are added as small spots about the apex of the sector (*15, 54*). It usually provides narrower, more clearly defined zones with less trailing than those formed by linear paper chromatography (*15, 54*). Paper strips tapered near the starting end are reported to exhibit some of these desirable features of radial flow in sectors (*135*). Diffusion gradients from the wash liquid improve certain separations (*169*).

An arrangement for the unexplored segmental flow in a pad of filter paper is illustrated by Figure 12. This arrangement is subject to variation in many ways. The tab, for example, may extend to the center of a thick pad of paper and may be insulated so that the chromatogram is formed as a series of concentric spherical zones.

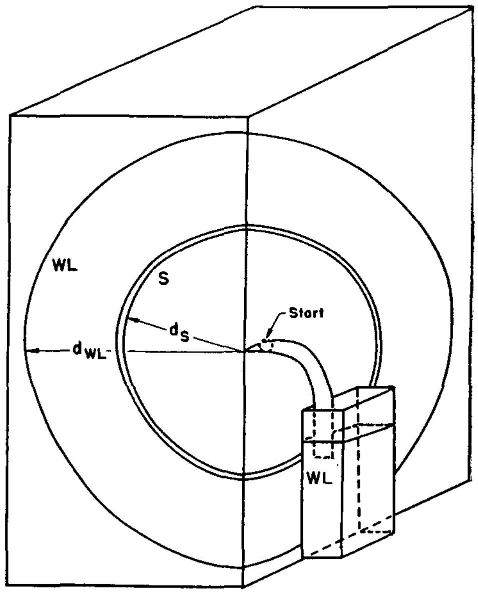

Figure 12. Untested Arrangement for Segmental (Spherical) Paper Chromatography

One of many possible arrangements for spherical flow in a segment of three-dimensional mass or solid angle

seg. $R_f = d_S/d_{WL}$

The resolving power of linear paper chromatography is similar to that of radial paper chromatography (*15, 135*). The resolving power of two-way paper chromatography greatly exceeds that of linear paper chromatography (*101*) (compare Figures 6 and 7). With certain amino acids, however, two-way paper chromatography does not resolve the mixtures completely. For the detection and isolation of the components of these mixtures, several two-way migrations have been performed with pairs of various solvents. Each two-way migration separates several components from the mixture, so that each component is isolated by at least one of the two-way migrations (*44*).

***R* Values and R_f Values.** The rate or distance of migration of a solute in a chromatographic system relative to the rate or distance of migration of the solvent provides the *R* value (Figure 10), which is widely employed for the description of substances and as a measure of sorbability. This value depends upon many conditions which should be controlled and described. These include: the concentration of the mixture; the time and the distance of migration; the nature, composition, and purity of the wash liquid; the temperature; the porosity of the medium; the nature and activity of the sorbent; the dimensions of the initial zone of the mixture; the dimensions of the migration system; and the distribution of the solvent in the migration system (*15, 31, 33, 84, 96, 139, 166, 183*).

From the theoretical viewpoint, the migration of a solute zone should be determined relative to the region of maximum concentration. As this region of maximum concentration is frequently difficult to detect, the frontal boundary of the zone is regarded as the reference point, and the corresponding *R* value is indicated by R_f. With many chromatographic systems, this boundary is diffuse. The location of the boundary, therefore, depends upon the sensitivity of the methods for the detection of the solute.

In similar chromatographic systems, the R values for particular solutes are subject to less variation if related to the R values of a similar reference substance, for example,

$$R_b \text{ of } a = R \text{ of } a/R \text{ of } b$$

This ratio of R values is a precise application of the chromatographic sequences so widely employed in qualitative, exploratory investigations. When the R values of two preparations are equal, when R_b of a = 1, a and b may be identical. This is a precise application of the mixed chromatogram or co-chromatogram.

R values determined with linear flow (Figure 10) and with radial flow from a narrow stream into a planar mass (Figure 11) have been indicated by the same symbol, R (*15*). As shown by Figure 12, R values may also be determined by segmental flow from a narrow stream into a three-dimensional mass. For careful work, all these R values should be distinguished by distinctive symbols—for example, lin. R, rad. R, and seg. R. If the migration systems have the same porosity and the same sorptive capacity, and if the distribution of the liquid in the three systems is uniform,

$$\text{lin. } R = (\text{rad. } R)^2 = (\text{seg. } R)^3$$

For sugars in filter paper lin. R was found equal to (rad. $R)^2$ (*15*). With migration systems of soft paper, however, the distribution of the solvent in the paper is not uniform (*183*); hence the above relationship is an approximation.

Electrochromatography. Differential electrical migration from a narrow zone of the mixture in electrolytic solutions was carried out in columns and in gels about 15 years ago and subsequently called electrochromatography. Adapted to use in moist paper about 5 years ago, this method has now been widely utilized in various fields, not only for the resolution of mixtures but also for the determination of various properties such as isoelectric points and complex formation (*2, 69, 104–106, 144*). There are many reasons for the widespread adoption of this technique—the earlier, extensive experience with the related paper chromatography; the numerous, sensitive methods for the detection, elution, recovery, and estimation of the separated substances already perfected with columnar and paper chromatography; the slight decomposition of labile substances such as proteins when migrating in a porous system with sorption at a minimum (*88, 89, 133*); the simplicity and economy of the apparatus (*154*); and the high resolving power for many mixtures that are difficultly separable by other methods.

Electrochromatography has been applied to the examination of two principal groups of substances—namely, small ions, both organic and inorganic (*36, 46, 75, 97, 125, 143, 144, 158, 162*), and large colloids, such as proteins and polysaccharides (*21, 52, 73, 88, 89, 108, 133, 154*). This diverse application has led to a complicated nomenclature. As applied to colloidal proteins, differential electrical migration in paper is called paper electrophoresis, zone ionophoresis, zone electrophoresis, electropherography, paper electropherography, and ionography (*105, 106*). If a distinction is to be made between ionophoresis and electrophoresis, based upon the size of the migrating particles, a collective term applicable to both ions and colloids is desirable. Because a narrow initial zone is employed, as in conventional chromatography, because sorption occurs in many of the migration media, and because sorption is the selective factor in many separations by electrical migration (*143, 162*), electrochromatography is the most apt of the terms now in use. Unfortunately, the adverb electrochromatographically contains 26 letters!

Several forms of electromigration apparatus are available commercially (*105, 106*). For research purposes, simplified forms of the apparatus may be constructed to suit each particular investigation (*40, 78, 144, 154. 160*). As in chromatography, the electrolytic solution and the stabilizing medium may be varied in numberless ways (*40, 78, 105, 106, 144, 158*). The common media are gels, porous beds, paper, and ion exchange resins.

With moist paper, two principal arrangements of the electrodes have been employed. Electrodes have been placed in separate reservoirs of the electrolytic solution in contact with the moist paper (*105, 106*), and they have been clamped directly to the moist paper (*144, 162*). With the former arrangement, both electrical migration and electro-osmotic flow of the solution transport the ionized or charged particles. As in the moving boundary method, the electro-osmotic flow of the solution (d_f) may be ascertained by the migration of a zone of an easily detectable, nonionized, nonsorbed substance added to the migration system (*144, 154*). The transport of the charged migrating particles by the electro-osmotic flow will be retarded if the particles are sorbed by the medium; hence the electro-osmotic transport of the particles will be the product of this flow (d_f) times the lin. R value of the particles determined chromatographically in the migration system. The distance of the migration due to electrical transport alone (d_e) will be the observed migration (d_o) corrected for the migration due to electro-osmotic flow; thus

$$d_e = d_o - Rd_f$$

With electrodes clamped to the paper, there is very little electro-osmosis, particularly with $0.1M$ organic acids as the electrolytic solutions (*144*). Alteration of the paper itself may also restrict the electro-osmotic flow (*78*).

The formation of well-defined zones depends upon careful control of many conditions such as the nature and concentration of the electrolytic solution, the nature and concentration of the mixture, the nature and the porosity of the stabilizing support, and the voltage (*144*).

The electrical mobility of the particles differs from the mobility in free or unstabilized solutions. This variation may be attributed to electro-osmosis, to sorption by the stabilization support, to the action of the support as a barrier which increases the distance that a particle must migrate, and to orientation of the solvent and electrolyte molecules at the interfaces between the support and the solution, thereby increasing the heterogeneity of the migration medium (*105, 106, 144, 154*). As in chromatography, the mobilities may be reported in relation to the mobility of some standard or reference substance (*52*).

Two-way electrochromatography in different solvents has been employed with inorganic and organic ions (*46, 133, 162*).

Crossed or transverse electrical current in one medium has been reported to provide a more selective migration system than one-way migration (*105, 106*). From the view that the resultant effect is the vector sum of two identical forces, this arrangement is similar to one-way migration in a potential gradient. Centrifugal or magnetic fields transverse to an electrical field has been proposed for the separation of racemic mixtures (*99*) and for the migration of neutral particle (*83*). Migration in dry paper has been observed (*75, 146*), and migration in living organisms (iontophoresis) opens many new fields for exploration (*65*).

Continuous electrochromatography with flow of solvent transverse to electrical potential has been improved and applied to the separation of ions (*145, 160*), dyes (*58*), and proteins (*24. 25, 72*). The theoretical boundary conditions have also been considered (*51, 173*).

ION EXCHANGE RESINS

Continued research on ion exchange substances has increased the number of these materials that are finding increased use in differential migration techniques (*123*). Resins with oxidation-reduction properties (*142*), with chelating properties (*59*), with ion-exclusion properties (*177*), and in the form of membranes (*180*) offer many possibilities for applications in analysis and in industry (*123, 172*). The electrochemical properties of these resins have recently become a subject of intensive investigation (*158, 159, 180*).

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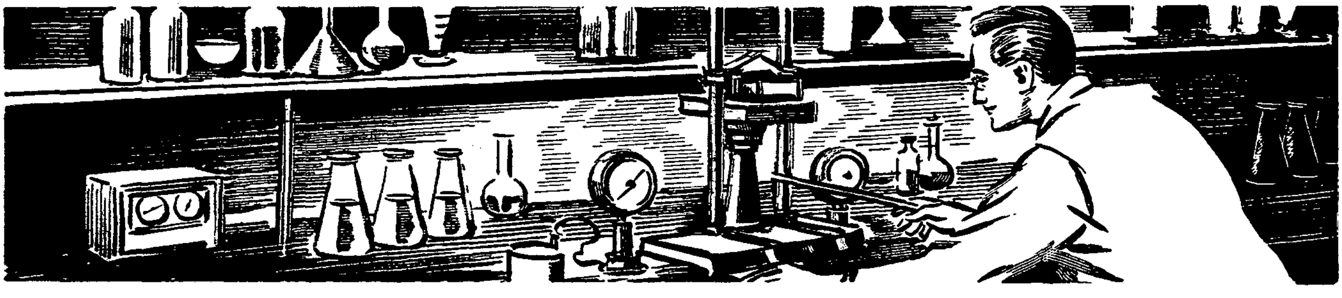

Distillation Analysis

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THIS review differs from its predecessors (*92*) in that no attempt has been made to list all the specific examples of the use of distillation for analytical purposes. Attention is confined to significant applications and to improvements in apparatus, procedure, or technique that are felt to be of general importance.

A study of an indexed compendium of abstracts of the literature on distillation covering a 7-year period (*94*) develops the conviction that the great majority of all papers on distillation are of present or potential interest to analysts. The only general exceptions are the papers dealing with the details of construction or operation of large scale equipment, and to a lesser extent the more specialized advanced theoretical treatments. All other papers are at least potentially useful as the basis for improving an existing analysis or devising a new one.

The major part of this review deals with the development of new apparatus and techniques for analytical distillation involving rectification with a column. In addition to citing the more important of these, it seems desirable to comment briefly on what is lacking, or what might have been published but did not appear. In other words, an attempt has been made to note what analysts might like to see published, as far as distillation is concerned. These ideas are presented with full knowledge that they are from a single point of view. Possibly this will stimulate discussion and progress.

There seem to be two prime needs. One is for simpler, less expensive but still effective, automatic or nearly automatic apparatus for general use. Possibly an entirely new approach to the problem is required. The second need is for a good practical laboratory manual giving definite and specific instructions for construction and operation for the inexperienced, for those who cannot afford to buy complete setups, and for those whose interest is of a short-term nature. The attainment of the first of these needs may be wishful thinking, but the second certainly is not. There is a wealth of scattered published information on practical techniques, and there are excellent discussions on the basis for these. The lack is in integration and reduction to practical terms. None of the published literature gives such information.

As far as the actual published literature is concerned, for the period November 1, 1951, to November 1, 1953, the high spots seem to be:

1. Distillation research and development activity has passed the high quality peak evident in 1951.
2. Apparatus developments of greatest interest are in rotary and spinning band columns for vacuum distillation, and in continuous laboratory columns.
3. There is concern about flooding and flow properties in packed columns, and in column behavior under vacuum.
4. There is continued interest in low temperature distillation.
5. The Natural Gasoline Association of America is active in a systematic, constructive way through a school, seminars, cooperative analysis programs, and the publication of standardized procedures.
6. A good deal is being published on the distillation of fatty acids and related compounds.
7. A surprising proportion of significant references are from foreign journals.

The importance of safety precautions and considerations, even in low temperature distillation, is brought out by explosions during distillation of chlorine dioxide (*7*), dinitrochlorobenzene (*34*), and performic acid (*115*).

GENERAL APPARATUS, PRINCIPLES, AND REVIEWS

Only a few descriptions of complete apparatus have appeared. One of these indicates European practice (*98*), two relate to automatic or mechanized apparatus (*28, 82*), and two others are specialized [porous bubble plates (*101*); metal column for corrosive mixtures (*74*)]. No completely new ideas are involved.

There are several general discussions of principles (*11, 39, 107, 108*). For those interested in making calculations of theoretical plates and reflux ratio, there are new papers involving finite reflux (*83*) and pole height (*121*), constant distillate composition (*40*), holdup (*79, 93, 124, 125*), and an elementary exposition of methods of calculating plates from composition and vapor-liquid equilibrium data (*96*).

Recent vapor-liquid equilibrium data have been indexed (*94*), and the exhaustive Horsley tables of azeotropes have now been put out as one of the *Advances in Chemistry Series* (*45*). The appearance of details on schizoid surface phenomena (*41*) is worthy of mention in connection with vapor-liquid equilibrium under vacuum. A new edition of the ASTM Standards has been published, as well as a 50-year index to the technical papers and reports of that society (*1, 2*).

PACKED COLUMN OPERATING VARIABLES AND TESTING

Considerable interest is evident in flooding and related phenomena. Dell and Pratt (*13*) have extended the range of an equation originally derived for liquid extraction columns, so that it is applicable to gas-liquid systems. Pratt (*84*) has reviewed wetted wall columns and given data and equations on the wetting of packing and on film resistance. Williamson (*117*) has described liquid distributors and splash eliminators. He also gives an equation, based on HTU considerations, for calculating the optimum velocity in a packed tower with gas film controlling. Several theses have dealt with flooding and flow distribution in packed towers (*43, 62, 65, 99*). Once again a modification of the Sherwood correlation has been shown to give satisfactory results (*73*), in an investigation of the effect of surface tension on flooding, when wetting agents and soaps were added to water passed countercurrent to air in a column packed with Berl saddles. The same article reviews the literature on flooding. Murch (*68*) has presented an equation for calculating HETP in terms of mass velocity of vapor, tower diameter and height, liquid density, viscosity and relative volatility, and packing shape-size constants. Ellis (*20*) proposes a somewhat similar formula. Kolling (*51*) has tabulated extensive performance data for packings of various types. A patent has been issued to Dixon (*17*) covering his method of flooding and operation with gauze packing.

Work on testing and performance has dealt mostly with operation at reduced pressure. Zuiderweg (*122*) suggests the use of *n*-decane–*trans*-decalin and *n*-hexadecane–*n*-heptyl benzoate as test mixtures in this field. Feldman and Orchin (*23*), after some extensive work on the separation of the 1- and 2-methylnapthalenes, now propose them for evaluation of vacuum columns. Haldenwanger (*33*) also suggests mixtures of 1- and 2-methylnaphthalenes for this purpose, and *p*- and *m*-xylenes as a test mixture when many plates are involved. Bliss *et al.* (*3*) use *o*-dichlorobenzene–*o*-diethylbenzene at low throughputs to demonstrate that the effect of temperature on the liquid film is the main cause of HTU variations when distillation pressure is changed from 18 to 50 mm. in a 3-inch tower packed with $^1/_2$-inch Raschig rings. Peters and Cannon (*77, 78*) have found that each of several packings behaves differently when studied at various pressures between 10 and 740 mm. They give the equation

$$G = K\left(\rho\,\frac{MP}{RT}\right)^{1/2}$$

for calculating maximum mass velocity in terms of a packing constant, K, the liquid density, molecular weight, pressure, temperature, and the gas constant. Hawkins and Brent (*37*) state that HETP changes but little as pressure is reduced from atmospheric to 20 mm. They use benzene-chlorobenzene and n-heptane–methylcyclohexane test mixtures in spiral screen and glass Raschig ring columns 18 mm. in diameter. Sugimura and Reynolds (*111*) have made similar studies in several types of packed columns, but results are inconclusive as to the effect of pressure.

Leva (*58*) has described the line of reasoning followed in development of a new ceramic tower packing in attempts to achieve high surface area and flooding velocity with minimum pressure drop. Other new packings have been described by Hayter (*38*), Shorland (*102*), and Teller (*113*). The latter ascribes an improved HTU to the relatively large holdup of the rozette-type packing, although superficial reasoning suggests the opposite effect. The counterbalancing effects of large holdup in prolonging the startup period, in reducing sharpness of separation at high reflux ratios, and in increasing undistillable residues in batch distillation, must be considered in an over-all evaluation of such a packing. Fuchs (*27*) points out the possible effects of the chemical nature and surface adsorption on HETP values, and explains differences of various packings on this basis. Romanet's work (*91*) on intermittent versus continuous take-off does not seem to settle this question. Many of the references on the effects of operating variables are to work on columns 2 inches or larger in diameter.

COLUMN ACCESSORIES

There are many of these, and they are ingenious, but little fundamental and integrating work has been done on them. The writers never cease to wonder at the continuing stream of articles on reflux divider devices. Miller (*67*) describes a device involving drainage from one or more fixed areas of a condenser. As usual, the functioning of this arrangement depends on clean condenser surfaces. Collins and Willcock (*10*) use a calibrated tube and orifice for a pilot scale column. Swarr (*112*) recommends simple tests and special study to obtain accuracy with proportioning pumps that are often used for reflux division in pilot columns. A metering chamber drained through valves controlled by meniscus movement (*12*) might serve as the basis for reflux division as well as for operation of a fraction collector. Piros and Glover (*80*) describe a liquid seal trap and pressure equalizing line applicable to reflux dividers. The use of glass valves to control small liquid flows is likewise worthy of consideration and possible adaptation (*30*), as is a solenoid ball valve controlled by a photorelay (*19*). George (*32*) describes a compact refluxing head for a large fractionating column.

There are many references on fraction collectors (*8, 16, 46, 55, 63, 87, 89, 104, 114, 118, 120*). Some are designed for chromatography but should be considered for automatic distillation apparatus (*42, 59, 97*). Four new publications on manostats have appeared (*14, 21, 36, 61*). Hancock (*35*) has described a controlled adiabatic jacket, and Pantages and Feldman (*75*) a removable packing support useful for glass columns. Glass tubes affixed with external electrically conducting coating have been advertised but not evaluated in a scientific publication. Mason (*64*) has published a reminder that flooding at the base of a column may be avoided by use of a separate line for returning reflux to the still. Garrison and Rolfson (*29*) have patented some automatic controls. Many of these column accessories are related to automatic controls.

LOW TEMPERATURE DISTILLATION, LIQUEFIED GASES, AND NATURAL GASOLINE ANALYSIS

The NGAA booklet (*72*) on specifications and test methods for liquefied petroleum gas was issued during 1951 but not reported in this review for that year. This association has continued its cooperative analysis program (*70*) and is operating a school for analysis (*71*) in natural gasoline plants. A book on light hydrocarbon analysis (*6*) was the outgrowth of similar work by the Butadiene Committee, Office of Rubber Reserve. Standard calculation procedures, sample calculations, and routine calculation sheets for low temperature distillation have been published (*52, 86*). Preston (*85*) has improved the method of correcting for vapor holdup. Legatski and coworkers (*56, 57*) have developed the absorption index procedure as a means of reducing the number of conventional analyses required for establishing the composition of natural gas. Metal valves and Teflon packing glands are recommended by Brown and Skahan (*5*). A vacuum isothermal vaporization method of analysis for hydrocarbon gas mixtures containing oxygen and nitrogen has been patented by Clothier (*9*). Two papers discuss refrigerant supply (*4, 110*). Fookson *et al.* (*24*) have evaluated Stedman packing in the distillation of hydrogen isotopes. Orrick and Gibson's (*74*) complete metal apparatus for low temperature distillation of corrosive materials is worthy of study for use in other connections.

VACUUM DISTILLATION, ROTARY DEVICES

Aside from the performance and testing data mentioned in a previous paragraph, the most interesting papers relating to vacuum distillation involve rotary apparatus. Murray and Schoenfeld (*69*) and Horn and Hougen (*44*) have used amplified distillation in a small spinning band column to separate alcohols from carnauba wax and to recover glycols from wool wax. Zuiderweg (*123*) makes a careful comparison of performance data and mass transfer in a spinning band column 6 mm. in diameter and a Vigreux column 11 mm. in diameter. The data show more pronounced loss of efficiency with decreasing pressure for the spinning band column than for the Vigreux. This seems contrary to the generally accepted idea that spinner columns are most effective under vacuum. Rotary cylinder columns or similar devices have been studied by Jost (*47, 48*), Gel'perin (*31*), and Kaarsemaker (*49*). Perry's patent (*76*) covers a rotatable brush fractionating column whose cooled center achieves thermal rectification, and eliminates droplet and rivulet formation on the outer wall. Apparently all rotary and spinning band columns to date have been designed empirically, with no effort to predict the dimensions, clearances, rates, etc., for optimum separation due to the several diffusional processes involved.

Smith (*106*) has patented a column packed with a perforated spirally rolled sheet of stainless steel in which relatively thick liquids are distilled. The entire column is arranged so that it may be rotated in a plane forming a 14° angle with the horizontal. Rotation of the pot also eliminates bumping. Radin (*88*) describes a simply constructed still pot shaking device. Several other papers (*66, 103*) describe magnetic stirring devices for prevention of bumping. Michell eliminates stuffing box problems by locating the rotor within the evacuated glass system while the magnetic field is generated outside. Foster and Green (*25*) use a similar arrangement for the magnetic drive of a spinning band column. Feldman and Pantages (*22*) suggests a small hot wire coil immersed near the bottom of a still pot to control bumping. A self-pumping still has been advertised but not described or evaluated in any published paper.

LABORATORY CONTINUOUS DISTILLATION

Three additional laboratory continuous columns have been described. Kiguchi's apparatus (*50*) also serves for batch distillation of 5- to 17-gallon charges. His column, 3 inches in diameter, with 100 inches of protruded packing, has 60 plates at low boilup rates, 40 plates near flooding, but only 23 to 31 plates in continuous distillation tests. Dimick and Simone (*15*) have constructed a perforated plate column 28 mm. in inside diameter with 25 plates above and 15 below the feed. Wilcox, Coulter, and Lloyd (*116*) give complete and detailed descriptions of glass equipment for continuous distillation. This includes methods for introducing feed, controlling feed rate, reboiler details, and a variety of reflux dividers. Start-up and shutdown procedures and methods of rate determination are given. Lloyd previously (*60*) had summarized the advantages and disadvantages of laboratory batch and continuous distillation, and a theoretical comparison has also been made (*95*). Krell (*53*) has published a review of continuous distillation in the laboratory.

MICRODISTILLATION

There are too many applications of simple and conventional microdistillation to permit mention of them. Piros and Glover (*81*) have patented a micro fractionating column of the rotary type. Dubowski and Shupe (*18*) have described a standardized apparatus for semimicro simple or steam distillation. Wolff (*119*) conducts tests for micro quantities of acetyl and formaldehyde by distillation from an asbestos absorbent. Sims (*105*) describes a micromolecular still in which one drop of sample is dispersed on a small glass wool pad suspended from the end of a quartz spiral in the axis of a small tubular furnace. A cathetometer is used to note movement of the spiral as the distillation progresses. Sherwin (*100*) employs a somewhat similar technique for separation of radioactive elements from carriers.

MISCELLANEOUS

Amplified distillation has been used by Murray and Schoenfeld (*69*) to secure sharp separation of high boiling materials in vacuum distillation. Nothing has appeared regarding the theory of amplified distillation. An analytical separation of metals by fractional distillation of their halides has recently been reported by Fowler (*26*). Similarly, germanium in coal ash (*109*) may be determined by steam distillation of the volatile chloride, and subsequent conversion to the oxide. Rollet (*90*) secured what is probably thermal rectification by using an empty column so placed that the lower side of the tube could be heated from below, while the upper side was cooled from above. A total reflux separation equivalent to about 90 plates per meter length was obtained with benzene–ethylene dichloride test mixture at total reflux in a tube 100 cm. long by 7.6 mm. in diameter. Kunzler (*54*) proposes constant boiling sulfuric acid as a material of precisely known composition for use as a primary standard in acidimetry.

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Ion Exchange

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A SURVEY of the literature on ion exchange during the past two years has shown a continued interest in the use of ion exchange techniques in many analytical chemical problems. An indication of the role of ion exchange in analytical chemistry is evident upon examination of a recent text written by Samuelson (*237*), entitled "Ion Exchange in Analytical Chemistry." This outstanding contribution reviews the theory and practice of ion exchange in its application to analytical chemistry and to many other allied fields. It is of particular interest in that Samuelson suggests procedures that have been investigated sufficiently so that they may be placed on a routine basis, thereby enabling the control analyst to conduct analyses with ion exchange with but a minor amount of exploratory research.

Although the interest in the use of ion exchange in analytical chemistry is rapidly increasing, the actual number of quantitative methods that are of general use are few. To date, the chief analytical uses for this technique appear to be divided among separations in biochemical analysis; separations of metallic complexes from one another and from materials not capable of forming complexes; concentration of dilute solutions; and the determination of total ionic concentration in various solutions, natural water supplies in particular.

In addition, several difficulties encountered with this technique have hindered the universal acceptance of ion exchange in analytical chemistry. Some of these difficulties are the impurities encountered in "run-of-the-mill" commercial resins; variations in results with various samples of the same commercial grade of ion exchange resin; and unfamiliarity with the general principles of ion exchange.

However, regardless of these difficulties, it has been generally accepted by those experienced with the technique that a considerable number of useful analytical procedures employing ion exchange can be developed if use is made of the available theory relating such functions as distribution coefficients, exchange capacity, ion valence, and pH.

REVIEWS

In addition to Samuelson's major contribution (*237*), several excellent reviews have appeared which encompass the properties, applications, and theories of ion exchange. Recent studies in England have been summarized by Kressman (*166*), Duncan (*81*), and Pepper (*219*). Osborn (*212*) has compiled an excellent bibliography on the use of exchangers in analytical chemistry. Special reviews on ion exchange in drug, fine chemical, and pharmacy applications have been prepared by Lesser (*178*) and Bücki (*48*). The Manchester Section of the Society of Chemical Industry (*62*), Kings College (*63*), and the Gordon Research Conference held conferences which reviewed recent developments in this country and abroad. Boyd (*35*), Bauman *et al.* (*16*), Kunin (*171*), and Cassidy (*56*) have written extensive reviews covering ion exchange theory and application. Tiselius (*278*), Basinski (*15*), Tompkins (*279*), and Samuelson (*239*) have summarized work in Europe.

THEORY

The development of the theory of ion exchange went through a period of consolidation in the past two years. Emphasis has been placed on the development of thermodynamic relationships in a form similar to those derived for soluble electrolytes. The role played by the polymer structure on ion exchange equilibria and physical properties of the system has been investigated by several workers. Glueckauf (*100*) and Duncan (*82*) have extended the recently developed theory of Gregor employing the concept that exchangers are similar to homogeneous solutions of similar concentration. Boyd and Soldano (*36*) have measured and calculated the osmotic free energies of exchange systems. Davies (*75*) has developed a theory relating the adsorption and swelling properties of weak base-type anion exchangers. Bonner *et al.* (*10, 31–33*) have determined equilibrium constants for several monovalent cation exchange systems using the Gibbs-Duhem relationship. Betts (*22*) developed a relationship for the exchange of ions in solutions of mixed electrolytes. The equilibrium for the exchange of organic bases with a carboxylic exchanger has been studied by Saunders (*245*). Pepper (*217–219*), Hale (*111*), and Kuhn (*170*) have reported on the influence of polymer structure on ion exchange reactions. The selective behavior of the carboxylic acid group of ion exchange resins has been discussed by Deuel (*77*). Bregman *et al.* (*37, 64*) have reported on the properties of phosphonous and phosphonic acid-type cation exchange resins.

The preparation of exchangers which show selective affinity for specific cations has been described by Klyachko (*161*). Vickery (*289*) has the correlated ion exchange elution data with stability of rare earth complexes. Partridge (*214*) has employed ion exchange resins as molecular sieves and has developed a concept of this phenomenon. Mysels (*205*) has made an attempt to explain certain pH changes occurring in colloid systems by means of ion exchange equilibria. Honda (*123*), Kagawa (*145*), and Kakihana (*147*) have determined equilibrium constants for several exchange systems. The theory of column performance has been developed by Vermeulen (*286, 287*) for aqueous and nonaqueous systems. Cherkin (*65*) calculated and studied a gradient elution procedure which reduces the tailing effects in chromatographic columns. Wheaton and Bauman (*298*) reported on the application of ion exclusion techniques for the separation of non- or weakly ionized substances from strong electrolytes.

NEW ION EXCHANGE MATERIALS AND METHODS

Developments of new ion exchange materials and techniques have followed well-defined patterns. So-called electron exchange polymers capable of undergoing oxidation and reduction reactions have been prepared and studied by Cassidy (*55, 57, 85*). Gregor *et al.* (*106*) reported on the properties of exchangers containing chelate groups. Ion exchange materials based on cottons were prepared by Guthrie (*109*). Phosphonic acid groups were introduced into a polymer by Daul and Reid (*73*). D'Alelio (*71, 72*) produced cation exchange resins from the sulfonation of styrene–aryl acetylene copolymers. Bodamer (*28–30*) described the preparation of permselective films of cation and anion exchange resins by impregnation of finely divided ion exchange particles into a polymeric matrix. Bodamer (*30*) also produced carboxylic cation exchanger from "popcorn" polymers of acrylic acid and polyolefinic materials. Bauman (*17*) synthesized quaternary-type anion exchangers from tertiary amines. Gapon (*95*) and Marconi (*191*) developed modified methods for the determination of total capacity of cation exchangers. Sasaki (*244*) employed a conductometric titration procedure to determine the capacity of cation exchangers. Minami (*196*) used electrometric methods to evaluate the effluent composition of cation exchangers used to separate hydrogen, rubidium, and cesium. Leick (*175*) studied several hydrogen-cycle ion exchange systems. Roberts (*227*) developed an ion exchange demonstration experiment for physical chemical laboratory. Calmon (*51, 52*) made use of the volume changes observed in low cross-linked cation exchangers as a measure of ionic strength and valence of ions in solution. Grunbaum (*108*) developed a capillary buret for reagent generation which employs ion exchange resins. Honda (*126*) used a high-frequency oscillator to locate chromatographic bands within the ion exchange column.

INORGANIC SEPARATIONS

Ion exchange resins have been employed for many new inorganic separations. Routine use of ion exchange resins has been reported by Spedding *et al.* (*61, 263*) and Tevebaugh (*274*) for rare earth separations. A continuous and automatic method was reported by Luigi (*188*) for the same purpose. Various improvements in these procedures were reported by Trombe and Loriers (*280, 281*). Vickery (*288*) compared the efficiency of various eluting solutions for ion exchange chromatography. A procedure for the separation of titanium, zirconium, and thorium was developed by Brown and Rieman (*40, 41*). Radhakrishna (*222, 223*) separated thorium from the rare earths. The separation of basic aluminum ions has been reported by Honda (*124*) while Kakihana (*146*) has developed a procedure for the separation of beryllium from aluminum. Lister (*182*) studied the solution chemistry of zirconium by means of ion exchange. Freund (*90*) used ion exchanger resins to separate zirconium from aluminum. Kraus (*164*) used an anion exchange resin to separate ferric sulfate complexes from aluminum sulfate. Pure protoactinium isotopes were prepared by Barendregt (*14*). Blasius (*23*) studied the borotungstate complexes using strong base anion exchange resins. The separation of molybdates of several heavy metals has been examined by Klement (*160*). Fisher and Meloche (*88*) have separated rhenium from molybdenum on strong base exchangers. The elution of niobium was studied by Huffman and Iddings (*133*).

A process for the recovery of gold from cyanide leach solutions has been reported by several British workers (*49*). Leden (*174*) proved the presence of anionic complexes in cadmium and copper solutions. Isomeric complexes of cobalt were separated by King and Walters (*157*). West (*296*) fractionated cobalt complexes. Salmon and Tietye (*235*) have studied the separation of tetra- and pentavalent vanadium ions in phosphoric acid solutions. Hering (*117*) has separated quantitatively traces of lithium from calcium. Ryabchikov and Bukhitiarov (*233*) used ion exchange chromatography to separate copper and iron. Iron complexes were investigated by Whitaker (*299*). Fronaeus (*91*) measured the equilibrium between nickel and acetate ions. Moore and Kraus (*199*) have separated cobalt and nickel in hydrochloric acid solutions using strong base anion exchangers. D'Ans and Blasius (*8*) have employed resins for the separation of cobalt and chromium salts. The separation of the cation complexes of chromium thiocyanates has been investigated by King and Dismuker (*156*). Similar studies have been reported by Samuelson (*238*) and by Yoshimo (*310*) for the separation of arsenic from iron. Rieman and Tendenbaum (*225*) have used strong base anion exchange resins for the separation of chlorides and bromides. Muto (*204*) removed interfering cations prior to a basic acid determination. Kraus (*163*) studied the anion exchange separation of the transition elements from manganese to zinc. He also examined separation of sulfuric acid from metal sulfates (*165*). A similar study was made on hydrochloric acid adsorption on strong base anion exchange resin (*162*). Interfering phosphates were removed by anion exchange resins prior to a calcium determination (*42*).

ORGANIC SEPARATIONS

The application of ion exchange resins has become routine for the purification and separation of the components obtained from various biological systems. Ion exchange resins have been used extensively for the fractionation of amine acids from various sources (*2–4, 9, 11, 13, 25, 34, 38, 39, 45, 53, 54, 56, 67, 78, 98, 102, 113, 114, 121, 129, 131, 135, 151, 172, 194, 198, 215, 216, 226, 234, 256, 265, 266, 270, 272, 276, 282, 283, 291, 306, 313*). Carsten (*53, 54*) and Stein (*266*) made complete analyses of the amino acid separations, while Baker (*13*) employed the technique for enzymatic resolution of proteins. A comparison of various methods of purification has been made by Sanger (*242*). Hirs (*118*) has employed volatile buffers to facilitate the concentration of the ion exchange fractionated amino acids. [Studies of nucleic and ribonucleic acids have employed ion exchange fractionation of these complex systems (*26, 66, 68, 74, 76, 89, 103, 107, 116, 119, 128, 183, 185, 187, 195, 232, 248, 275, 290*)]. Dinucleotides were resolved after separation from monucleotides (*153, 184, 186, 254, 260*). Adenosine phosphates obtained from yeast have been studied by means of ion exchange (*6, 18, 27, 79, 80, 136, 150, 154, 202, 203, 253, 257, 312*). Hydroxyproline, proline, and peptides were isolated and fractionated from collagen (*132, 167*). Lysozyme was fractionated on carboxylic cation exchange resins (*249, 273*). Purines, pyrimidines, polypeptides, and other nitrogenous materials were studied by ion exchange (*142, 173, 241, 268, 293*). Bacterial metabolic products were also prepared for study after an ion exchange treatment (*115*). The effect of electrolytes on the hydrolysis of urea by urease was examined by Kistiakowsky *et al.* (*158, 159*). Pantothenic acid in urine has been determined after ion exchange chromatographic separation (*18, 70*). Erythrulose phosphate and other metabolic products were purified by exchange treatment (*60, 138, 144, 261*). Gardell (*96*) used a cation exchanger for the separation of glucosamine and galactosamine. A weak base exchanger was used by Salmon (*236*) in order to concentrate *l*-ascorbic 1-C^{14} acid. Serine and sarcosine (*197*), cytochrome (*50, 207*), and pipecolic acid (*200, 311*) have been purified and isolated by ion exchange. Chlorogenic acid was isolated from apple fruit by Hulme (*134*). Roseman *et al.* (*230*) employed ion exchange to remove interfering ions during the biosynthesis of hyaluronic acid. Rosenberg (*231*) employed ion exchange to isolate a growth factor from chicken tissue. Exchangers were used to decolorize plant extracts (*247*) and to isolate porphobilinogen from urine (*297*). Degradation products from amylopectin (*277*), inosital phosphates (*259*), and hypoxanthine and inosine acid (*252*) were fractionated and isolated by means of ion exchange. Pituitary hormones have been purified by ion exchange techniques (*169, 181, 221, 225, 300*). Xanthople-6,7-C^{14} has been fractionated and purified by Dixon (*79*) and Anher and Boehne (*7*). Xylose has been isolated from an enzymatic reaction by strong base anion exchange resins (*120*). Polysaccharides were subjected to an ion exchange treatment prior to isolation by Hough (*130*). Khym and Zill (*155*) studied the separation of sugars on strong base anion exchange resins. Windsor (*304*) studied the separation of aminoadipic acid.

MISCELLANEOUS ANALYTICAL APPLICATIONS

Ion exchange has been applied to a variety of miscellaneous analytical problems in recent years. Jindra *et al.* (*139–141*) have employed ion exchange for the determination of sulfamides, sympathomimetric amines, and antihistaminics. Motl (*201*) used strong base ion exchange resins for the determination of atebrine. Narcotics were evaluated by Levi and Farmils (*179*) and Hilty and Grant (*104*). Yampol'skaya (*308*) developed methods for the determination of a wide variety of pharmaceutical preparations using cation exchangers. Bücki and Furrer (*48*) devised an analytical method for the determination of alkaloids. Ergothioneine was measured in blood by strong base anion exchange resins (*193*). McCoy (*189*) applied exchangers to water analysis. Samuelson *et al.* (*5, 93, 94, 112*) developed analytical methods for the separation of aldehydes and ketones from acids and alcohols in the determination of formic acid in the presence of formaldehyde, and also studied the effect of oxidizing agents on ion exchange materials. Samuelson and Schramm (*240*) and Syllmann (*271*) developed a method for measurement of total salt concentration which employed strong base anion exchangers. Oda *et al.* (*210, 211*) and Parkinson (*213*) used ion exchange to separate and concentrate vitamin B prior to analysis. Steinback and Freisse (*267*) and Greenbaum *et al.* (*105*) have used an anion exchanger to prepare standard caustic solutions. Salts in organic acids and bases (*12*) and microanalysis of the salts of organic acids (*284*) have been determined using cation exchange resins.

Sweet *et al.* (*269*) have used exchangers for the determination of alkali metals in insoluble silicates. Ammonia and magnesium in urine are separated and concentrated on cation exchange resin prior to their estimation (*309*). Boron analysis may be facilitated by means of ion exchange (*44, 192*). Galacturonic acid determination by ion exchange techniques has become a standard procedure (*305*). Vitamin assays have been improved by various ion exchange techniques (*246, 295*). Sugars and carbohydrates have been isolated and analyzed by cation (*262*) and anion exchangers (*20, 58, 59, 152, 208, 209, 220, 228, 229, 307, 314*). Various plant extracts and flavors have been concentrated and isolated on carboxylic cation exchange resins (*137, 143, 301–303*). Gums have been purified by deionization in order to remove acids and bases (*1*). Nitrogenous extracts of haddock were fractionated by Shewan *et al.* (*255*). The reaction products from the carboxylation of resorcinol (*110*) were separated on strong base anion exchange resins. Coenzyme A was purified on similar resins (*264*). Antibiotics were studied by ion exchange methods (*180, 258, 285*). Medicinal preparations are described which make use of ion exchange fractionation (*313*). A direct method for the determination of acid-base relationships in blood sera has employed cation exchange resins (*84*). Gaudie and Rieman (*97*) and Kubo and Tsutsumi (*168*) have suggested an ion exchange technique in the determination of phosphates.

Honda (*125*) has described the preparation of indicating resins for pH studies. Methods for the preparation of laboratory columns have also been described (*19, 21, 43*). Several procedures for sulfate determination have been suggested (*92, 127, 148, 206*). The application of exchange to measurement of total acidity or basicity of solutions has been discussed (*176, 177, 190*). Copper has been determined in mineral oils by concentration on cation exchangers (*46*). The adsorption of inorganic salts from solvents was studied by Katzin (*149*). Blasius and Wachtel (*24*) detected polar pyridine iodide complexes by their cation properties. Disposal of radioactive cations from waste solutions was investigated using cation exchangers (*99*). High purity hydrogen peroxide was prepared by cation exchange (*83*). Special deionization procedures for blood sera employing mixtures of exchangers have been described (*86*). Weinstock and Boekelheide (*294*) employed basic exchangers as catalyst for Hofmann degradation reactions, thereby simplifying analytical procedures on the products. Electrometric titration of chloride may be improved by using a half cell containing a hydrogen-silver exchange resin (*100*). Sansoni (*243*) has studied oxidation-reduction reactions on exchanger beds. A "zebra" column consisting of layers of various types of exchangers has been found useful for the preliminary evaluation of unknown solutions (*122*). Schubert (*250,251*) has reported on the determination of complex stability by use of ion exchange techniques. Excess acid has been removed by ion exchange prior to analysis (*87*). Waldock (*292*) has determined the infrared structure of several functional groups in ion exchange polymers.

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Extraction

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THIS review covers primarily the papers dealing with analytical extraction which have appeared since the 1952 review of this series. Much of the work covered has already been mentioned in other general or specialized reviews (*36, 90, 125, 148, 150, 165, 171, 177*) on extraction or some phase of it but from a different standpoint. No claim is made here of complete coverage of all aspects of the subject. Extraction in some form has long been a part of many analytical procedures and accordingly is often given little emphasis in the description of the work. It is obviously impossible to learn of all such procedures, as they are not commonly indexed in abstract journals under the heading of extraction or even under a related subject.

The particular phase of extraction covered perhaps can best be defined in terms of the purpose for which the extraction is to be made. If it is to be made and used as a method to learn something, either qualitatively or quantitatively, of the nature of an unknown, it properly comes within the scope of this review. Processes designed for large scale purification are not usually covered, as they are so well covered in the reviews in *Industrial and Engineering Chemistry* (*171*). Only in cases where the reasoning or theory has a bearing on procedures which might be used in analytical extraction are such papers mentioned. However, when the process is designed to permit purification of sufficient material for structural study or further analysis, it properly falls within the scope here intended.

No attempt is made to cover the field called "Partition Chromatography," although this certainly is a countercurrent extraction process, irrespective of whether or not solid-liquid or liquid-liquid extraction is responsible for the effect. However, this type of extraction is a specialized field and has been covered in a separate review of this series.

A survey of the literature since the review of 1952 (*35*) was written does not indicate major progress in different types of apparatus, although a number of papers describing new apparatus have been published. It would appear that extension of the usefulness of extraction for analysis does not now depend so much on apparatus as on a better understanding of systems and the choice of solvents or discovery of complexing agents, so that much higher selectivities can be reached. Definite advances along this line are to be reported in several fields, most notably in systems for the separation of inorganic substances and for the separation of peptides. It is thought by Weaver and collaborators (*180*) that liquid-liquid extraction offers the most promising approach to the problem of the separation of the rare earths. Systems with β values of 1.6 between adjacent members of the atomic series (*145*) apparently have been developed by the use of tributyl phosphate. Those familiar with countercurrent distribution will recognize this as a rather easy separation.

In trying to review the recent literature on analytical extraction the writer has been impressed by the many confusing facets of the subject and the interrelation of the various factors which have a bearing on whether or not a given extractor and procedure are the best for the problem. All too often a publication describes a new apparatus and procedure but on the basis of its use for a restricted purpose has gone on to recommend its general use without giving sufficient consideration to the interrelation of the various factors.

In attempting to give the proper balance in this review to the many claims which are to be found in the literature, the following flow sheet has been prepared. In it most of the considerations are listed which contribute to the science of extraction and which necessarily form the basis for the choice of any particular extraction procedure.

1. Systems	
Stability	Distorting effect of solutes
Partition ratio	Recovery of solute
Partition isotherms	Speed of interchange
Selectivity of system	Complexity of mixture
Rate of break of dispersions	Molecular size and complexity of solutes
2. Apparatus	
Single stage	Cost of apparatus and availability
Discontinuous	
Continuous	Selectivity
Multiple stage	Reproducibility
Discontinuous	Labor involved
Countercurrent	Time involved
Discontinuous	
Continuous	
3. Analysis	
Direct weight	Titration
Spectroscopic	Time for analysis
4. Purpose	
Removal	Amount of pure substance desired
Fractionation	Purity required

The most important consideration from almost any point of view in any extraction process is the choice of a suitable system. Obviously, the ideal system would be one so selective that a single contact would accomplish the full purpose of the extraction, thus eliminating the need for extensive apparatus. This often is the case but, when not, more extensive apparatus is brought into play in order to increase the over-all selectivity of the process.

SYSTEMS

The choice of a suitable system is indeed one of the major difficulties in the use of extraction. Unfortunately, the compounding of systems cannot be done very successfully on the basis of theoretical predictions, although some correlations have been made (*58, 84, 139*). Experience in compounding systems is of the greatest assistance, but unfortunately there is no substitute for an actual experimental trial. In general, however, in an unknown field a good system may be found more quickly than the best solvent for purification by recrystallization or the best adsorbent for resolution of an unknown mixture by chromatography.

A system as treated here includes not only the liquids but all sorts of additives incorporated to produce a desired effect. These agents include salts for salting out or salting in, complexing agents like the hydrotropic agents such as the sulfonic acids, and coordinating agents or chelating agents such as those so widely used in inorganic analysis. In the past few years many satisfactory systems have been compounded for different separations. In the hope that a list of many of these will be helpful in suggesting other systems, a number of tables of different systems which have proved useful in various separations during the past two years are given.

Where the separation desired warrants a careful study of systems in order to reach the highest selectivity, an approach such as that suggested by Engel and collaborators (*51*) will prove helpful if the system involves combinations of three or more solvents.

A survey of the tables reveals considerable use of very simple systems. Where these fail to give the required selectivity or behavior, more complex systems have been devised. Buffers have proved especially helpful. In many cases careful studies of complex formation (*55, 62, 63, 151*) have been made. This is a familiar approach to inorganic chemists (*90*) and now has become very important in separations with the rare earths.

In comparing the relative use for analytical extraction which has been made of the strictly discontinuous process, with that of the continuous processes, a survey of Tables I to V will be found very instructive. Nearly all the applications of the past two years have been made by countercurrent distribution (CCD), except in the inorganic field, and here simple extraction has been the choice. Most of the papers refer to some application of countercurrent distribution rather than to attempts to improve the procedure. This has not been true for attempts involving the continuous column approach. For a short account of countercurrent distribution reference (*36*) may be consulted. For a more detailed account, the excellent review of Rauen and Stamm (*150*) will be found very useful.

APPARATUS

During the past two years a number of continuous extractors designed for extraction for removal purposes have been reported. None of them offer new principles but many offer technical improvements of a practical nature.

Napoli and Schmall (*132*) and Kamphausen (*102*) describe apparatus for extraction of solids. Gage *et al.* (*56*) describe a laboratory wet grinder which can be used also for extraction. A microextractor set up also for steam distillation has been described by Connolly and Oldham (*33*) and one for extracting at reduced pressures by Bick and Clezy (*15*). Extractors in which the solid is extracted with the cold condensate have been described by Parks (*142*) and Herian and Moignard (*81*). All-

Table I. Inorganic Compounds

Solutes Separated	System	Apparatus	Ref.
Metal thiocyanate complexes	Tributyl phosphate, H_2O	...	(*123*)
Subgroup VII elements	Pyridine, 4*N* NaOH	...	(*60*)
Zirconium, hafnium	Benzene, various β-diketones, aqueous $HClO_4$ soln.	...	(*117*)
Pitchblende residues, ionium	Tributylphosphate, aqueous, HNO_3, $Ca(NO_3)$	...	(*144*)
Ionium, scandium	Dibutoxytetraethylene glycol diethyl ether, aqueous NH_4NO_3, HNO_3	...	(*144*)
Ionium, uranium	Ethyl ether, aqueous $Al(NO_3)$, NaAc, HAc	...	(*144*)
Uranyl nitrate	Dibutyl carbitol, pentaether, H_2O	...	(*57*)
Ferric chloride	Amyl acetate, 7*N* HCl	...	(*170*)
Th	Benzene, thenoyl trifluoroacetone, HNO_3 solns.	...	(*124*)
8-Quinolinol	Aqueous buffer, chloroform	...	(*128*)
Antimony	Ethyl acetate, H_2O, oxalic + citric acids	...	(*182*)
Nb and Ta	Xylene, 8*M* HCl, methyldioctylanine	...	(*118*)
Nb and Ta	Diisopropyl ketone, aqueous H_2SO_4, HF	...	(*168*)
In	Ethyl ether, aqueous HI	...	(*94*)
Group III B metal halides	Ethyl ether, aqueous halogen acids	...	(*93*)
Zn dithizone	$CHCl_3$ or CCl_4 and H_2O	...	(*92*)
Ce	Ethyl ether, 5*N* HNO_3	CC[a]	(*18*)
Metal bromides	Ethyl ether, HBr	...	(*17*)
Rare earths	Tributyl phosphate, nitric acid	SC[b]	(*180*)
Rare earths	Tributyl phosphate, HCl	CCD	(*145*)
Uranium perchlorate	Ethyl ether, perchloric acid	...	(*100*)

[a] Continuous countercurrent.
[b] Stage continuous.

Table II. Peptides

Solutes Separated	System	Apparatus	Ref.
Actinomycins	MeBu ether, sodium naphthalenesulfonate soln.	CCD	(*22*)
Actinomycins	Ethyl ether, 5.6% HCl	CCD	(*24*)
Actinomycins	MeBu ether, 30% urea	CCD	(*23*)
Rhodomycins	Butanol, 0.1*N* phosphate	CCD	(*20*)
Rhodomycins	Butanol-ether, HCl soln. (pH 3)	CCD	(*21*)
Oxytocin	2-Butanol, 0.5*N* Aqueous HAc	CCD	(*147*)
	2-Butanol, 0.01*M* ammonia	CCD	(*147*)
Desulfurized oxytocin	2-Butanol, water	CCD	(*175*)
Bromine oxidation products of oxytocin	2-Butanol, 0.5% acetic acid	CCD	(*157*)
Hog vasopressin	1-Butanol, 0.09 *p*-toluenesulfonic acid	CCD	(*149*)
Oxidized oxytocin	1-Butanol, 6% acetic acid	CCD	(*130*)
Partial hydrolysis products of vasopressin	2-Butanol, 0.1*N* acetic acid	CCD	(*50*)
Synthetic oxytocin	2-Butanol, 0.1*N* acetic acid 2-Butanol, 0.01*N* ammonia	CCD	(*49*)
ACTH	2-Butanol, 0.2% aqueous trichloroacetic acid	CCD	(*183*)
ACTH	2,4,6-Collidine, water	CCD	(*82*)
ACTH	2-Butanol, 0.5% aqueous trichloroacetic acid	CCD	(*19*)
ACTH	2-Butanol, 0.1% aqueous trichloroacetic acid	CCD	(*112*)
Benzoyl peptides	Ethanol, H_2O, $CHCl_3$, cyclohexane	CCD	(*97*)
Hydrolyzate of gramicidin	1-Butanol, dilute acetic acid	CCD	(*96*)
Peptide from *B. subtilis*	1-Butanol, 0.1*M* phosphate buffer	CCD	(*5*)
Nisins	Methanol, butanol, acetic acid, water, NaCl, NaAc	CCD	(*13*)
Nisins A, B, C, and D	Methanol, 1-butanol, acetate buffer	CCD	(*14*)
Licheniformins	Phenol, dilute HCl	CCD	(*27*)
Micrococcin	Ethanol, acetic acid, $CHCl_3$, CCl_4, H_2O	CCD	(*75*)
Clupein, salmine	1-Butanol, lauric acid, NaAc buffer	CCD	(*151*)
Pipsyl derivatives from peptides	Various organic solvents with water	CCD	(*119*)
Pipsyl derivatives from peptides	Various organic solvents with water	CCD	(*166*)
Bacitracins	Pentanol, butanol, phosphate buffer	CCD	(*134, 136*)
Bacitracins	2-Butanol, 3% acetic acid	CCD	(*43*)
Amino acids from bacitracin	2% HCl, phenol	CCD	(*41*)
DNP derivatives of bacitracin	2-Butanol, 3% acetic acid, $CHCl_3$, water	CCD	(*42*)
Polypeptin	2-Butanol, isopropyl ether, dilute HCl	CCD	(*74*)
Tyrocidines	Methanol, $CHCl_3$, 0.1*N* HCl	CCD	(*9*)
Tyrocidine A derivatives	Methanol, benzene, $CHCl_3$, 0.1*N* HCl	CCD	(*10*)

Table III. Lipides

Solutes Separated	System	Apparatus	Ref.
Lipides from placenta	Mixtures of CCl_4, $CHCl_3$, CH_2Cl_2, CH_3OH, and H_2O	CCD	(*32*)
Lipides from brain	CH_3OH, CCl_4, H_2O	CCD	(*31*)
Phospholipides from ox brain	Pet. ether, ethanol, H_2O	CCD	(*121*)
Linseed phosphatides	Hexane, CH_3OH, H_2O	CCD	(*122*)
Uridine-5-pyrophosphate derivatives	Phenol, sulfate buffer	CCD	(*141*)
Me esters of higher fatty acids	Pentane, hexane, nitromethane, nitroethane	CCD	(*28*)
Peroxides of methyl linoleate	Pentane, hexane, ethanol, H_2O	CCD	(*186*)
Urinary estrogens	CH_3OH, CCl_4, H_2O, ethanol, cyclohexane, ethyl acetate, H_2O	CCD	(*127*)
Steroid mixtures	Cyclohexane, ethyl acetate, ethanol, water	CCD	(*51*)
Adrenal cortex hormones	Pet. ether, water		(*146*)
Cholesterol	Heptane, 90% ethanol	CCD	(*1*)
Cephalins, DNP.-ethanolamine, DNP - serine	Benzene, 5*N* HCl, methyl butyl ketone, citrate buffer	CCD	(*4*)
Phospholipins	Pet. ether, acetone, ethanol, H_2O	CCD	(*138*)

Table IV. Alkaloids

Solutes Separated	System	Apparatus	Ref.
Alkaloids of veratrine	$CHCl_3$, CCl_4, 2*M* acetate buffer	CCD	(*108*)
Desacetylneoprotoveratrine	Benzene, 2*M* acetate buffer	CCD	(*109*)
Alkaloids of veratrine	Cyclohexane, benzene, 2*M* acetate buffer	CCD	(*110*)
Zygadenus alkaloids	$CHCl_3$, 2*M* acetate buffer	CCD	(*115*)
Zygadenus alkaloids	Benzene, phosphate buffer	CCD	(*114, 116*)
Neogermitrine	Benzene, 2*M* acetate buffer	CCD	(*54*)
Alkaloids of veratrine	Benzene, phosphate buffer	CCD	(*140*)
Alkaloids of veratrine	Benzene, 2*M* acetate buffer	CCD	(*59*)
Alkaloids of veratrine	$CHCl_3$, acetic acid, H_2O	CCD	(*133*)
Alkaloids of veratrine	0.5*N* HCl, $CHCl_3$	CCD	(*169*)
Germbudine, isogermidine	Benzene, 2*M* acetate buffer	CCD	(*126*)
Wilforgine	Benzene, hexane, 2% HCl	CCD	(*11*)
Wilfortrine	Benzene, 1.8% HCl	CCD	(*11*)
Wilforgine	Benzene, hexane, 2% HCl	CCD	(*12*)
Ryanodine	Ethyl ether, water	CCD	(*106*)
Corynanthein	Ethyl ether, citrate buffer	CCD	(*65*)
Tar bases	Cyclohexane, phosphate-citrate buffer; $CHCl_3$, phosphate-citrate buffer	CCD	(*61*)
Pyridine alkaloids	*tert*-Amyl alcohol, various buffers	CCD	(*6*)
Garraya alkaloids	$CHCl_3$, phosphate-citrate buffer	CCD	(*184*)

Table V. Miscellaneous Organic Solutes

Solutes Separated	System	Apparatus	Ref.
Porphyrins	Ether, HCl	CCD	(*67*)
Aromatic amines	Cyclohexane, H_2O, Ag^+	. . .	(*62*)
Cresols	Cineole, cyclohexane, H_2O, Ag^+	. . .	(*63*)
Maple lignin	Butanol, trisodium phosphate soln.	CCD	(*66*)
Carbobenzoxyglutamic esters	Ethyl ether, phosphate buffer	CCD	(*159*)
α-Lipoi7 acid	$CHCl_3$, 0.5*M* phosphate	CCD	(*143*)
α-Lipoic acid	Organic solvents, buffer	CCD	(*154*)
Pyruvate oxidation factor	Ethyl ether, 0.5*M* phosphate buffer; ethyl ether, HCl (pH 2)	CCD	(*68*)
Lipoic acid	Benzene, 50% acetic acid	CCD	(*155*)
α-Lipoic acid	Benzene, 50% acetic acid	CCD	(*156*)
Cohumulone	2,2,4-Trimethylpentane, phosphate-citrate buffer	CCD	(*158*)
Cohumulone	Iso-octane, 0.5*M* phosphate buffer	CCD	(*87*)
Cardiac glycosides	Ethanol, water, $CHCl_3$	CCD	(*79, 173*)
Antibiotics from basidiomycetes	$CHCl_3$, phosphate buffers	CCD	(*104*)
Antibiotics from basidiomycetes	Ethyl ether, hexane, methanol, H_2O	CCD	(*103*)
Antibiotics from basidiomycetes	Benzene, hexane, H_2O	CCD	(*48*)
Flavines	1-Butanol, 0.02*N* HCl	CCD	(*153*)
Rhizopterin	1-Butanol, 0.02*N* HCl	CCD	(*152*)
Vitamins B_{12}, B_{12b}, etc.	Phenol, CCl_4, H_2O	CCD	(*101*)
Transformation products of vitamin B_{12}	Benzyl alcohol, H_2O	CCD	(*137*)
Biocytin	$CHCl_3$, cresol, dilute HCl	CCD	(*185*)
Gliotoxin	$CHCl_3$, H_2O	CCD	(*99*)
2,4-D metabolic products	Ethyl ether, phosphate buffer	CCD	(*85*)
Germination factor	*tert*-Butanol, pet. ether, acetone, H_2O	CCD	(*25*)
Antibiotics from cephalosporium	Hexane, isopropyl ether, acetone, phosphate buffer	CCD	(*26*)
Magnamycin	Benzene, acetate buffer	CCD	(*178*)
Mycomycin	$CHCl_3$, phosphate buffer	CCD	(*29*)
Streptomycin	Pentasol, aqueous buffered stearate	CCD	(*55*)
Antimycins	Benzene, pet. ether, 80% ethanol	CCD	(*162*)
Formic acid	Me isobutyl ketone, water	. . .	(*176*)
Various solutes	1-Pentanol, water 2-Methyl-1-propanol, water	. . .	(*64*)
Various organic bases	Liquid paraffin, phosphate buffer	. . .	(*45*)
Higher fatty acids	Various combinations of methanol, heptane, iso-octane, acetic acid, formamide, and acetonitrile	CCD	(*2*)
Conjugated bile acids	Heptane, isopropyl ether, acetic acid, 2-butanol, 3% acetic acid, heptane, 97% acetic acid	CCD	(*3*)
Carotenoids from orange juice	Pet. ether, 99% methanol	CCD	(*44*)
Various aldehydes from lignin	Various organic solvents, water	CCD	(*16*)

purpose extractors have been described by Kratz and Frank (*111*), Hemmings (*79*), and Iffland (*89*). The latter has an adjustable elbow on the overflow tube which permits adjustment of the level of the liquid in the extraction chamber. Schmall *et al.* (*161*) have designed an extractor for the determination of the salts of organic acids. Extractors were designed especially for use in the purification of radioactive substances by several workers (*69, 98, 124*). Liquid-liquid extractors with stirrers in the extraction chamber to promote interchange were described by Holliman (*86*), Henry and Sorba (*80*), and Dobson and Randall (*47*). The latter also has a built-in rapid evaporator for concentrating the extract. An extractor with a diffuser plate and arranged for use under reduced pressure has been given by Heftmann and Johnson (*78*). Other extractors (*46, 72, 88, 105*) have been described.

Less interest has been shown in the design of new equipment for extraction for fractionation purposes. For fractionation purposes the interest appears largely to have been directed toward the search for suitable systems for countercurrent distribution as Tables I to V show.

Metzsch (*125*) has described an automatic all-glass 200-tube countercurent distribution train, which has a number of different features from the one described by Craig and collaborators (*39*) and mentioned in the last review of this series. Tschesche, Grimmer, and Neuwald (*174*) have described a hand-operated train made from glass. It requires individual transfers. Hickey (*83*) has described a mechanical robot for operating a countercurrent distribution train. Its design is different from that designed by Craig and collaborators (*39*) and may well appeal to one who builds his own robot and fraction collector. It operates by vacuum drive in order to avoid the danger with organic solvents resulting from an electric spark.

Short and Twigg (*164*), Short (*163*), Bock and Meyer (*18*), and Spence and Streeton (*167*) have described continuous countercurrent extractors for analytical purposes. All have made use of a spinning center pole in the column. Extractors of the stage continuous type have been reported by Fischer and Jübermann (*53*), Nagata, Eguchi, and Yokoyama (*131*), and Weygand, Wacker, and Dellweg (*181*). The latter is an interesting modification of the countercurrent distribution machine which provides for continuous flow of the lighter solvent.

Certain of the advantages of the discontinuous process for liquid-liquid extraction for fractionation have been mentioned elsewhere in this review. That similar advantages might be found in the liquid-solid type of extraction had also been suggested by Craig and collaborators (*38*). Recently Morris (*129*) has found this approach to be promising and has built a countercurrent distribution apparatus especially for liquid-solid extraction. At each stage the liquid is transferred by decantation through a filter.

Granick and Bogorad (*67*) designed an apparatus to be inserted in the Beckman spectrograph for determining partition ratios rapidly when analyzing countercurrent distribution runs.

In countercurrent distribution the most informative distribution pattern is one which is based on direct weight analysis. When properly done, this analysis need not be particularly time-consuming. Two procedures (*40, 77*) for accomplishing this have recently been reported.

THEORETICAL CONSIDERATIONS

After reading many papers dealing with the theory of countercurrent extraction, this reviewer has the impression that many research workers are not really aware of the basic differences between the strictly discontinuous process and the continuous process. Merely evaluating a continuous process in terms of theoretical plates calculated on the basis of the changes in concentration produced in an arbitrarily chosen mixture does not satisfactorily explain the basis for the effect the column has produced. The term "countercurrent distribution" has even been applied more than once erroneously to a continuous process.

In countercurrent distribution either phase is caused to move in a strictly stepwise manner. This is not a "cascade" and the difference as far as separation is concerned is more than superficial. In countercurrent distribution each transfer is made only after complete equilibrium (or a known degree of disequilibrium) is reached. Discrete volumes of a constant amount of the phases are moved on to the next contact each time. The ranges of concentration of the solutes are known and the partition isotherm has a real meaning. These factors are all vital in permitting a theoretical distribution curve to be drawn.

With the continuous process a different state of affairs exists. Equilibrium in the sense of the discontinuous process is never reached. Some operating stage, often far short of equilibrium as far as partition is concerned, determines the separation. It is therefore a rate process, in the sense that its efficiency may largely depend on the relative rates the different solutes approach true equilibrium. These may or may not be different and may even permit separation of solutes with very similar partition ratios, (*37*, p. 220; *91, 181*). All solutes do not approach equilibrium at the same rate in a given system.

Even more serious with continuous columns may be the effect of solute concentrations building up in the column when the solute is fed in continuously. This can contribute toward an easier separation, but usually it has the opposite effect. Phase shifts are usually undesired.

These effects are not easy to evaluate in the continuous process, but they are undoubtedly reflected in the well-known variation a given continuous countercurrent extractor will show when its plate efficiency is measured with different solutes, different systems, different concentrations of solutes in the same system, and different flow rates of the solvents. Further examples of such variations can be found in recent studies with continuous extractors (*8, 30, 52, 163, 164, 167*). Even sound can have an effect (*73*).

The rate of approach to equilibrium is a basic phenomenon in extraction which merits much further study, in spite of the fact that the literature on this subject in chemical engineering is voluminous (*34, 120, 172*). How variable this is with different solutes and solvents can be shown experimentally (*7*) in a very simple manner.

Of all the solutes and systems thus far studied by countercurrent distribution, by now a considerable number, as Tables I to V show, among organic solutes the vast majority easily reach essential equilibrium with only the few gentle shakes which the distribution machine provides. Only the penicillins (*7*) with buffered solutions seemed to be slow. This fortunate state of affairs does not appear to hold for the complexes of certain inorganic ions (*90, 91, 95*). In the extraction of zinc dithizone (*92*) from aqueous buffers with chloroform, shaking for a matter of minutes was required. When carbon tetrachloride was used, less time was required. Irving, Bell, and Williams give a good account of this observation and show the desirability of studying the approach to equilibrium with the solute first in one phase and then in the other, as had previously been done with the penicillins (*7*) in the author's laboratory.

The many confusing aspects of the phenomenon of the transport of solute from one phase to the other are still best explained on the basis of the two-film theory (*37, 172*). Simple diffusion cannot explain the resistance to transport. Ward (*179*) has presented data pertinent to this problem in studies on the kinetics of adsorption at liquid-liquid interfaces. With certain systems—e.g., hexane, water—and with long-chain fatty acids as solutes a newly formed interface would not reach its maximum interfacial tension until several minutes had passed. The effect was attributed to an "entropy activation barrier."

From the practical standpoint as applied to columns attempts to accomplish better interchange have been made with pulse extraction columns (*30, 52*) and with a spinning tube in the column (*18, 163, 164, 167*). HETP values as low as 0.6 inch have been obtained but not with very high total number of plates in the column.

Perhaps also from the practical standpoint it would be well to point out that the glass countercurrent distribution train can be conveniently used for the same type of extraction as these columns were designed to accomplish. For example, a hand-operated unit with twenty tubes of the design given (*39*) (available commercially from H. O. Post, 6822–60th Road, Maspeth, N. Y., in any size desired) and arranged for recycling with ten tubes in the upper row and ten in the lower row is ideal for this purpose. The alternate or double withdrawal procedure given (*37*, p. 202) can be used and fresh portions of solute added to the appropriate tube on each transfer to maintain desirable solute concentrations. For this purpose the excellent formulas developed by Scheibel (*159, 160*) can be used for calculating the amount of solute to be added in order to reach and maintain the proper balance. This method of operation gives the well-known triangular pattern which Scheibel and Klinkenberg (*107*) have treated.

In spite of its discontinuous nature, a favorable system with phases which separate in 30 seconds will permit 20 extract and 20 raffinate phases to be collected per hour. Even with the smallest distribution apparatus which is built for 10 ml. in each phase, this would mean a throughput of 200 ml. of each phase per hour. This compares favorably with continuous small laboratory extractors with this number of plates. With the distributors built for 100 ml. in each phase, the throughput would be 2 liters of each phase per hour. If this is not sufficient capacity, there is no mechanical reason against building distributors which hold 1 liter of each phase per tube. The advantage of such a distribution apparatus over the continuous columns would be that it operates on the basis of true equilibrium and a constant number of actual stages. It would also be very easy to increase or decrease the number of stages if required. Moreover, solute concentration effects could be observed and readily studied at any stage of the process.

The Podbielniak centrifugal extractor is a very efficient tool and is widely used in industry for production. One of its major advantages is the speed of extraction. Although even the smallest model, the "Pup," is somewhat beyond the range of this review, many readers will find the excellent study by Barson and Beyer (*8*) of the characteristics of the Pup of great interest.

As regards the mathematics of countercurrent distribution, several papers may be cited. Newton and Abraham (*135*) give equations for calculating theoretical curves. Hecker (*76*) has given a mathematical treatment and comparisons with the continuous process. Correlations of numbers of stages, β values, yield, and purity were made. Bland, Hillis, and Williams (*16*) have given a rather extensive mathematical treatment of these same considerations.

A general mathematical treatment for continuous countercurrent processes of all types has been given by Kuhn (*113*).

When countercurrent distribution is used for a separation, it is usually best to try to operate so that a symmetrical distribution curve is obtained—i.e., at complete equilibrium and in a concentration range which gives a nearly linear partition isotherm. On the other hand, when it is not practical to operate this way, many useful separations can be made in spite of the deviations.

The deviations can even be exploited. Weygand, Wacker, and Dellweg (*181*) used this approach in separating the hydrolysis products of desoxyribonucleic acid. The train was operated at disequilibrium. In the separation of the bacitracin polypeptides (*43*) the system was deliberately overloaded in order to produce a skewed pattern and thus obtain a higher yield of bacitracin A of high purity. However, for analytical purposes conformance to ideality is definitely to be preferred.

Deviation from the linear partition isotherm seems to be caused by association of solute molecules as given by the equilibrium $S \rightleftharpoons (S)_n$. Higher concentrations favor the formation of associated molecules, $(S)_n$. The difficulty as far as extraction is concerned is caused by the fact that the equilibrium is not the same in the two phases. With acidic or basic substances a buffer added to the system will usually help to produce a linear isotherm, probably because a high proportion of ionized molecules, S^+ or S^- molecules, exists and these scarcely partition in the organic phase. The net effect amounts to a lowering of the effective concentration and a more linear isotherm is favored.

Any solute added as part of the system which does not interfere otherwise and which associates strongly with the solute may help to give a more linear isotherm. With acidic solutes a good additive for the system is glacial acetic acid. The reasoning here is that the complex $S.(HAc)_n$ is predominantly formed and $(S)_n$ or $S_n.(HAc)_n$ repressed. Since there are so many HAc molecules available in both phases in equilibrium, the over-all effect amounts to that of the partition of simple S molecules. Irrespective of the validity of this reasoning, glacial acetic acid has permitted linear partition isotherms with the higher fatty acids (*2*), and both conjugated and unconjugated bile acids (*3*).

A similar type of reasoning has played a role in the development of complexes for partitioning inorganic solutes (*90*). Here buffers and strong acids are often used. Golumbic (*62*) and Golumbic and Weller (*63*) have used complex formation with silver ion in the attempt to develop selective systems for aromatic amines.

As a practical consideration it may be well to ask the limits of the present stage of development of analytical extraction and its over-all selectivity. There are bright points and others rather discouraging. For this reason the outlook would not be too bright if extraction were the only tool available. The same, however, would hold true for chromatography or any other separation approach. It is only when extraction is properly integrated with the other approaches that it finds its maximum effectiveness. Examples of this are to be found in the work with lipoic acid (*155, 156*), oxytocin (*49*), ACTH (*19, 111*), the carotenoids from orange juice (*44*), and others.

Individual cases of high selectivity are to be found in work on B_{12} (*101, 137*), tyrocidines (*9*), bacitracins (*43*), vasopressin (*149*), and actinomycins (*23*). Here separations were obtained, although slight structural changes in molecules of molecular weight 1000 to 1500 were the only differences. With the peptides the differences often resulted from the substitution of one single amino acid residue for another.

The insulin studies (*70, 71*) are interesting in this connection. The method of partial substitution (*71*) plainly showed beef insulin to have a molecular weight in the range of 6000, yet it could be fractionated by countercurrent distribution and a component B separated from the major component A. B was found to differ from A by having only five amide groups, whereas A contained six. All other analytical data, including quantitative amino acid analyses, were identical.

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Organic Microchemistry

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DURING the past 2 years there has been a steady flow of papers dealing with quantitative organic microanalytical methods and apparatus. The number of publications in European and Japanese journals has increased, while publications in American journals seem to have declined.

Methods for determining microgram quantities have become numerous and the classification of methods into macro, micro, and ultramicro appears to be crystallizing, with semimicromethods being absorbed mostly in the micro groups.

OXYGEN

Several papers of interest on the determination of oxygen have appeared during the past 2 years. All deal with modifications and sources of error in the Schutze-Unterzaucher carbon reduction method, which is being adopted rapidly by laboratories throughout the country.

One of the chief sources of error in Unterzaucher's modification of Schutze's method has been the interference of hydrogen, especially when samples with low oxygen content are analyzed. To eliminate this source of error Campanile *et al.* (*34*) included in their unitized apparatus a palladium thimble which permitted the hydrogen to be removed from the combustion products by diffusion. This permitted the sensitive iodometric titration to be retained. Sample weights used ranged from 5 to 50 mg., depending on the oxygen content, and the results were both accurate and precise.

Holowchak and Wear (*72*) proposed a manometric method which eliminates the error due to hydrogen. The carbon monoxide and hydrogen are oxidized by copper oxide, the water is removed by a dry ice trap, and the carbon dioxide is collected in a liquid nitrogen trap and then measured manometrically. Dundy and Stehr (*44*) employed a gravimetric determination of the carbon dioxide formed by the iodine pentoxide oxidation as a means of eliminating the large hydrogen error occurring in the analysis of petroleum products with low oxygen content. Gouverneur *et al.* (*60*) eliminated high blanks and other sources of error by determining the carbon dioxide volumetrically and improving the purity of the transport gas. Hinkel and Raymond (*70*) used the same approach in their semimicromethod. The carbon dioxide was absorbed in $0.05N$ alkali, the carbonate precipitated with barium chloride, and the excess alkali titrated with $0.025N$ acid. Sample weights ranged from 15 to 350 mg. for samples with oxygen contents of 50 to 0.05%. Analysis time was about 45 minutes. Unterzaucher (*183*) reviewed his micromethod for oxygen, first published in 1940, and gave a comprehensive list of references.

Iron impurities in the carbon are believed by Otting (*138*) to cause reduction of the quartz tube and give rise to blank values. A new type of high temperature furnace for maintaining the carbon at 1120° C. was described by Steyermark *et al.* (*174*). The heating element was a $^3/_8$-inch Inconel pipe with insulation around the outside.

A new method for detecting oxygen in organic compounds, based on thermal decomposition and detection of the resulting carbon monoxide or dioxide, was proposed by Goerdeler and Domgörgen (*56*). A method for determining small quantities of oxygen in nitrogen gas, an important consideration in oxygen analyses, was described by Lourenço (*121*).

CARBON AND HYDROGEN

In the determination of carbon and hydrogen, the greatest amount of study has been directed toward substitutes for lead dioxide for removing oxides of nitrogen. Kainz (*85*) changed from oxygen to air for oxidation of the sample and consequently was able to replace the lead dioxide with a copper section and improve his results. The copper had to be regenerated with hydrogen about every 12 runs.

Lévy and Cousin (*115*) recommended the use of dry manganese dioxide, previously suggested by Belcher and Ingram. Ingram (*77*) reported further on the use of manganese dioxide to remove not only oxides of nitrogen but also chlorine and sulfur dioxide, and has measured the conversion of nitrogen to the dioxide in the rapid combustion method.

Lévy and Cousin (*115*) and Wurzschmidt (*192*) reported the use of silvered pumice in place of silver wire or gauze. Saturated potassium dichromate in concentrated sulfuric acid was used by Mitsui (*127*), who found this approach satisfactory for samples with NH_2 groups, but NO_2 groups caused the hydrogen values to be high. Klimova and Korshun (*100*) impregnated dry silica gel with $0.02N$ potassium dichromate in concentrated sulfuric acid until the gel was almost wetted and used this material between two layers of magnesium perchlorate as a dry absorber for oxides of nitrogen.

Berret and Poirier (*19*) introduced several modifications into the carbon and hydrogen determination, one of which was the elimination of the lead dioxide. Korshun (*106*) and de Vries and van Dalen (*41*) reported on the empty-tube method; the former had difficulty in obtaining complete combustion, while the latter authors suggested the use of spark ignition of the vapors to overcome incomplete combustion and explosions. A rapid combustion method using the conventional tube filling was reported by Israelstam (*79*). Copper instead of lead dioxide was used to eliminate errors due to oxides of nitrogen.

Carbon and hydrogen methods for compounds containing silicon were reported by Klimova *et al.* (*101*), containing fluorine by Throckmorton and Hutton (*181*), containing alkali salts by Sirotenko (*168*), and containing tin and lead by Colaitis and Lesbre (*38*).

A number of workers have discussed new apparatus and automatic combustion. These include Mitsui (*125, 126*), who used dry ground joints and no wiping of the absorption tubes, a stationary sample burner, and a hydrogen correction based on the relative humidity and temperature of the room.

Sakamoto (*150*) discussed automatic apparatus for both the carbon and hydrogen and the Dumas nitrogen determinations. Korshun and Sheveleva (*107*) found that silver did not remove all the sulfur unless it was heated to near 700° C., that results with and without platinum catalyst were equally good, and that sulfur was retained by the rubber tubing used to join the combustion and absorption tubes. This latter effect was eliminated by the use of ground joints. Teflon joints were used by Kirsten (*97*) to join the combustion and absorption tubes. Among the several modifications of the carbon and hydrogen apparatus proposed by Sugiyama and Furuhashi (*176*) was the use of ground joints and the elimination of wiping of the absorption tubes. Hozumi *et al.* (*73*) described a modified apparatus and the use of a constant air current for combustion. Niederl and Whitman's method of combustion in an atmosphere of nitrogen was tested by Mangeney (*123*) with good results.

Two wet-combustion procedures for carbon were reported by Peters and Gutmann (*144*) and Thorn and Shu (*180*). The former authors' method was for determining radioactive carbon in material with a low carbon content and the latter was a titrimetric procedure.

Kawano *et al.* (*90*) described the preparation of reagents for Pregl's method, Thompson (*179*) described a calculator for selecting correct sample weights based on the expected analytical values, and Kasagi (*89*) discussed the application of sequential tests to reduce the number of analyses required for establishing the empirical formulas of organic compounds.

NITROGEN

Dumas. Recent trends in the Dumas method for nitrogen were the modification of the apparatus to permit more rapid burning of the sample and sweeping of the nitrogen into the nitrometer and the use of a mixture of carbon dioxide and oxygen to obtain better sample combustion. Shelberg (*164*) has made a number of modifications in the Dumas method which obviate slow sample burning and slow gas flow rates. The two-combustion-tube technique has a number of advantages and apparently gives reliable results with an analysis time between 10 and 20 minutes. Gysel (*64*) combined his previously published method with that of Zimmermann and obtained precise results which appeared to be insensitive to the burning rate. The stationary furnace was maintained at 800° to 850° C. and the sample burner at 950° C. Compounds containing sulfur were most difficult to burn. Mitsui and Tanaka (*128*) also modified Gysel's earlier method by adding a special nitrometer, using a copper boat, increasing the length of the copper oxide section, and placing the shortened copper layer in two sections.

Ingram (*78*), Alford (*1*), and Dirscherl *et al.* (*42*) all recommended the use of oxygen to aid in the combustion of the sample. In Ingram's method the oxygen prepared electrolytically was mixed with carbon dioxide and the mixture swept through the tube at 15 to 20 ml. per minute. The combustion tube contained only copper for removing the oxygen and the analysis time was about 20 minutes. The method proposed by Alford was more conventional, except for the use of pure oxygen for combustion of the sample. This method proved reliable for refractory heterocyclic compounds. An apparatus for mixing the carbon dioxide and oxygen in any desired proportion was proposed by Dirscherl *et al.* and hopcalite was found necessary if the copper section was located in the front of the tube filling. Kirsten (*95*) claimed that free oxygen in the presence of the copper oxide caused nitrogen oxide retention errors. He recommended the use of nickel oxide because it can be used at higher temperatures and does not liberate oxygen on heating, as does copper oxide. Pagel and Oita (*139*) discussed the errors in the Dumas method and particularly those due to air absorption.

The preliminary collaborative study of the Dumas method by the Association of Official Agricultural Chemists (*135*) showed a great variability in procedures throughout the country but little difference in accuracy and precision that could be associated with specific steps or techniques used by the various collaborators. Long furnace temperatures higher than 750° C. produced more precise results for the samples containing N—N and N—O bonds. Results obtained by the newer procedures proposed by Shelberg, Zimmermann, and Kirsten compared very favorably with those by the more conventional procedures, but too few collaborators used these new methods to permit a very reliable comparison.

Four articles have been published on carbon dioxide generators, one by Childs and Moore (*36*) on a modified Poth-type generator, and one by Konovalov (*104*) on preparation of the Kipp generator. Parkin *et al.* (*140*) and the British Standards Institute (*26*) discussed the use of solid carbon dioxide as the gas source.

Kjeldahl. The most prominent notes with regard to the Kjeldahl method for nitrogen have been the effect of the temperature of the digestion mixture on the digestion time and recovery of nitrogen and the design of new distillation apparatus. In the collaborative study reported by Lake (*110*) it was shown that the temperature could be raised by adding potassium sulfate to 410° C. without causing loss of nitrogen. The method that proved satisfactory for petroleum oils was 15 to 500 mg. of sample, 3 grams of potassium sulfate, 0.1 gram of mercuric oxide, and 4 ml. of concentrated sulfuric acid plus 0.5 ml. of acid for each 100 mg. above 100 mg. of sample with digestion for 1 to 1.5 hours at a temperature not greater than 380° C. The results indicated that the temperature should not be far below this value. Ribas and Vázques-Gesto (*147*) found that refractory heterocyclic compounds could be digested in 30 minutes if 3 grams of potassium sulfate in 2 ml. of sulfuric acid with mercury and selenium catalysts were used. The sealed-tube method of White and Long was used for ultramicroanalysis by Grunbaum *et al.* (*62*). A digestion temperature of 450° C. produced good recoveries, whereas temperatures of 470° C. and higher caused some decomposition of the ammonia.

Fish (*50*), Konovalov (*105*), Pepkowitz (*142*), and Ogg and Willits (*137*) all reported on the analyses of materials containing N—N and N—O linkages. Fish used reduction with zinc and hydrochloric acid in acetic acid or methanol, while Konovalov heated the materials in sealed tubes with hydriodic acid. The iodine liberated was fixed with red phosphorus and removed by boiling with sulfuric acid. Pepkowitz found that azide nitrogen could be determined if sodium thiosulfate was added to the sample before the sulfuric acid. The collaborative work reported by Ogg and Willits showed that about half the analysts obtained good results for compounds with N—N and N—O linkages by refluxing with hydriodic acid prior to digestion, whereas the results of the other analysts were low. As all analysts were following the same procedure, it must be concluded that some step or direction given in the method was not sufficiently well defined. Marzadro (*124*) claimed to be able to distinguish between various forms of nitrogen in heterocyclic compounds on the basis of results obtained by the Dumas-Zimmermann method and by a modified Kjeldahl procedure.

Titrimetric methods for determining nitrogen without distillation were proposed by Harvey (*66*), Lestra and Roux (*112*), and Llacer (*117*). The first two were based on the titration of liberated iodine with sodium thiosulfate, and the last method used the technique of Marcali and Rieman.

Seligson and Seligson (*162*) substituted discarded penicillin bottles for Conway cells and determined the nitrogen with Nessler's reagent. Slavík and Smetana (*169*) used Nessler's reagent to determine the ammonia liberated by enzymic reactions, the ammonia being absorbed in a tuft of glass wool soaked in 4*N* sulfuric acid.

The British Standards Institute (*29*) has published specifications for the micro-Kjeldahl digestion and distillation apparatus. Distillation apparatus, both micro and semimicro, was the subject of papers by Kirsten (*91*), Jenden and Taylor (*80*), Sickels and Schultz (*166*), Sheers and Cole (*163*), and Nógrády (*131*).

An interesting modification of the Van Slyke method for the microdetermination of amino nitrogen was proposed by Hussey and Maurer (*75*). The gases evolved were swept through a chromic acid–alkaline permanganate absorption train to remove oxides of nitrogen and the nitrogen gas was caught and measured in a micronitrometer.

SULFUR

Collaborative studies (*134, 136*) have been made of the more common micromethods for determining sulfur, including Carius, Parr, and catalytic combustions and both volumetric and gravimetric determination of the sulfate formed. The Carius and catalytic methods were about equally good, were more widely used, and appeared to be better than the Parr bomb procedure. More precise results were obtained by the volumetric than by the gravimetric method tested. Specifications for the micro Grote combustion train for sulfur and the halogens have been published by the British Standards Institute (*28*). Zimmermann (*194*) defended and elaborated on his method for sulfur, which involves reduction by potassium, distillation of the hydrogen sulfide, oxidation with iodate, and titration of the excess iodate. Kirsten and Carstens (*98*) claimed that errors occurred during the decomposition of the sample in Zimmermann's method and that these were approximately compensated by errors in the titration. Another titrimetric method for determining hydrogen sulfide or sulfide sulfur in microgram quantities was proposed by Dunicz and Rosenqvist (*45*). The method was based on the oxidation by alkali hypochlorite in highly alkaline solution.

Belcher *et al.* (*15*) determined sulfate alkalimetrically after precipitation with 4-amino-4 -chlorodiphenyl to eliminate errors due to nitrates or halides. In the titrimetric determination of sulfate with rhodizonate indicator Scalamandre and Guerrero (*154*) suggested adjusting the solution to less than pH 4 to eliminate phosphate interference.

Szekeres *et al.* (*178*) proposed a wet-digestion procedure using dichromate and nitric acid to convert sulfur to the sulfate, followed by gravimetric determination as the barium salt. Oda *et al.* (*133*) combined Stragand's method for sulfur with the usual carbon and hydrogen determination to produce a procedure for simultaneous determination of the three elements. Fischer (*49*), using an electron microscope, studied the effect of precipitating conditions on the nature of the barium sulfate crystals.

A spectrophotometric method for determining microgram amounts of sulfur in plant materials, etc., was described by Johnson and Nishita (*81*). The method involves the reduction of sulfates to hydrogen sulfide with hydriodic acid, formic acid, and red-phosphorus, and the conversion of the hydrogen sulfide to methylene blue.

Toennies and Bakay (*182*) and Grassner (*61*) reported turbidimetric methods for determining microgram quantities of sulfur. The former authors used a glycol–ethyl alcohol–water system to stabilize the barium sulfate suspension and were able to determine accurately as little as 3γ of sulfur.

A rapid combustion process for sulfur and halogens was described by Belcher and Ingram (*14*) and an improved quartz tube combustion apparatus by Peters *et al.* (*143*). The effect of varying conditions on the combustion of sulfanilamide in the Grote apparatus was described by Sundberg and Royer (*177*).

HALOGENS

In the collaborative studies on the determination of chlorine and bromine conducted by Steyermark and Faulkner (*172*) and Steyermark and Garner (*173*), better results were obtained by the Carius method of combustion followed by gravimetric determination of the halide. The preliminary study (*172*) showed that most of the collaborators were using either Carius or catalytic combustion methods and that these were preferable to the Parr bomb method. In the second study the results favored the Carius over the catalytic method tested, in both accuracy and precision. Specifications for a halogen and sulfur combustion train (Pregl) have been published by the British Standards Institute (*27*).

Although considerable work is still being done to devise titrimetric procedures for the halogens, no single method has gained sufficient favor to make it outstanding among the many methods proposed. Mercurimetric titration seems to be gaining in favor, and Jureček and Večeřa (*83*) have reported that with diphenylcarbazone as indicator, acidity under normal conditions has no deleterious effect on the results.

A new approach to argentometric titration reported by Hasselmann and Laustriat (*68*) recommended illuminating the solution with a narrow light beam during titration. The color of the pencil of light changed sharply from colorless or yellow to red at the equivalence point. For argentometric titrations, Dean *et al.* (*40*) recommended the use of polyethylene glycol 400 as a protective colloid. Rao and Shah (*146*) modified the Zacherl-Krainick wet-digestion method to permit the alkalimetric determination of the halogens in compounds containing nitrogen and sulfur. Another volumetric procedure proposed by Flaschka (*51*) required an ethylenediaminetetraacetic acid titration of nickel liberated from ammoniacal nickel tetracyanide by the silver salts. Nutten (*132*) found the mercuric oxycyanide method preferable to the direct alkalimetric method for halogens. Belcher and Goulden (*13*) tested silver, mercurous, and mercuric iodates for the determination of the chloride ion and found the three to be relatively comparable, with errors up to 2%. The iodate liberated by the chloride ion was titrated iodometrically.

Decomposition of the halogen-containing material with an alkali metal was investigated by Lohr *et al.* (*118*) and Kainz and Resch (*86*). The former authors used sodium metal in a nickel bomb and found the gravimetric analyses more accurate than the volumetric method; the latter used potassium in a glass tube and followed this with a Volhard titration.

Kainz (*84*) also proposed a procedure for bromine involving disintegration with potassium, followed by oxidation and iodometric titration. Simultaneous determination of chlorine and bromine was accomplished by Lévy (*114*) by combining argentometry and potentiometry. Bromine values had to be corrected by a value related to the quantity of chlorine present. A rapid potentiometric method for low concentrations of chloride ion employing a double silver–silver chloride electrode system was proposed by Blaedel *et al.* (*21*). Kirsten (*96*) made the oxygen and combustion products from a dry catalytic combustion react with hydrogen to effect more complete absorption, and give a higher concentration of halide with less foreign ions. A potentiometric determination was recommended. Cheek (*35*) and Pirt and Chain (*145*) applied the Conway microdiffusion technique to the determination of halogens, the latter authors using fuming nitric acid with silver nitrate to liberate the bound halogen. Gordon (*58*), after liberating the halogen with permanganate oxidation, applied a more sensitive colorimetric modification of the Conway microdiffusion technique. Another colorimetric method based on precipitation of chloride as mercurous chloride and measurement of the excess mercury was proposed by Staemmler (*171*). An apparatus for rapid combustion of compounds containing halogens and sulfur was described by Belcher and Ingram (*14*) along with suggested procedures for completing the determinations.

Zacherl and Stockl (*193*) recommended the use of bromine–glacial acetic acid as absorbent in the Leipert method for iodine and also advised heating the solution after reduction of the bromine with formic acid. Lein and Schwartz (*111*) discussed the use of ceric sulfate–arsenious acid reaction for the microdetermination of iodine, while Bosch and Rubia Pacheco (*22*) recommended that photometric measurements of iodine be made in carbon disulfide solution rather than in water.

The micromethod for fluorine proposed by Belcher *et al.* (*11*) involves fusion with alkali metal in a nickel bomb, titration with thorium nitrate, and back-titration of a comparison solution with standard sodium fluoride.

Three papers by Ballczo and Kaufmann (*7–9*) deal with a method for the determination of microgram quantities of fluorine and its application. They recommended the addition of methylene blue to the alizarin sulfonate indicator to increase the sharpness of the end-point color change.

OTHER ELEMENTS

Three methods for determining microgram quantities of phosphorus have been described by Harvey (*67*), Nakamura (*129*), and Schaffer *et al.* (*155*). All three are spectrophotometric procedures involving phosphomolybdic acid. In Schaffer's method the phosphomolybdic acid is extracted from the reaction mixture with octyl alcohol and determined by capillary spectrophotometry. A new microprocedure for phosphorus has been proposed by Ma and McKinley (*122*).

Methods for determining selenium in organic compounds were described by Gould (*59*), who completed the analysis titrimetrically, and by Kan (*88*), who used a gravimetric method. Bricker and Sweetser (*25*) in the determination of arsenic determined the end point of the titration spectrophotometrically at 320 mμ. The use of absorption in the ultraviolet for the detection of photometric end points seems to be an unexplored field and offers the advantages of eliminating indicators and indicator errors as well as the necessity of titrating to an exact end point. A comprehensive review of methods for determining metals in organic compounds was made by Belcher *et al.* (*12*), and both gravimetric and colorimetric micromethods for alkali metals were described by Duval (*46*). Van Etten and Wiele (*187*) proposed the use of ion exchange resins for determining organic salts.

GROUP ANALYSIS

Sodium thiosulfate was shown by Franzen *et al.* (*52*) to react with ethyl iodide under the conditions of the alkoxyl or alkylimide analysis, whereas the extent of the reaction with methyl iodide was considerably less. The difference in the reactivity of the two iodides was suggested as a means of distinguishing between the two. According to Huang and Morsingh (*74*), fully methylated dibenzyls have an anomalous behavior in the Zeisel method, in that they liberate methyl iodide although no methoxyl is present.

Kirsten and Stenhagen (*99*) studied the Kuhn-Roth method of C-methyl groups and proposed certain changes to improve the method. Three new apparatus for determining unsaturation by catalytic hydrogenation were described by Savacool and Ullyot (*153*), Vandenheuvel (*185*), and Schoniger (*156*). Micromethods for carbonyl groups were described by Bennett *et al.* (*17*), Schöniger and Lieb (*159*), and Schöniger *et al.* (*160*).

Determination of carboxy groups in aromatic compounds by decarboxylation was discussed by Beroza (*18*). Smith *et al.* (*170*) described the determination of acids, bases, and esters in small sealed tubes or serum bottles. The technique is versatile and promises to have many applications. Microgram quantities of fatty acids were titrated potentiometrically by Grunbaum *et al.* (*63*) and the fatty acids in serum were determined by Kaiser and Kagan (*87*).

A spectrophotometric micromethod for polyunsaturated fatty acids was described by Herb and Riemenschneider (*69*). Van Etten (*186*) described a reliable yet simple procedure for the microdetermination of saponification equivalents. Methods for the microdetermination of sulfhydryl groups in proteins were proposed by Kolb and Toennies (*103*) and by Sahashi and Shibasaki (*149*). Determination of aromatic hydroxyl groups with dibromoaminophenol was described by Shishikura (*165*). Brunner and Thomas (*33*) found that phenolic acetates hydrolyze rather rapidly during hydrolysis of the anhydride in the acetylation method of hydroxyl analysis. They recommended the use of 20- to 80-mg. samples and only a 3-minute hydrolysis.

APPARATUS

No attempt has been made to include references to all microapparatus described during the past 2 years. In general, only those pieces having a fairly direct relationship to the methods already discussed are included.

Two automatic combustion apparatus (*116, 126*) as well as a high temperature furnace for organic elemental analysis (*93*) have been described. The British Standards Institute published specifications for platinum, nickel, and porcelain crucibles (*30*) and for combustion boats, sheath, and contact stars (*31*). Accessory apparatus for the combustion of hygroscopic liquids (*57*) and for aqueous solutions of organic compounds (*82*) were described. Stainless steel absorption tubes (*109*) were used in place of glass tubes in the semimicrodetermination of carbon and hydrogen. Two apparatus for determining the molecular weight of volatile materials (*39, 130*) and a modified Signer apparatus (*188*) were described.

Two articles on microburets include descriptions of a high-precision buret (*54*) and the construction and calibration of simple semiautomatic microburets (*184*). Micropipets (*6, 10, 20, 37, 157, 161*) of various design and operation have been described.

Balances. Quartz fiber balances, their construction, maximum load, sensitivity, reproducibility, and application have been the subject of four papers (*4, 24, 108, 152*). Preference of the analyst for certain numbers has been shown by a statistical study (*65*) to be the cause of errors in weighing with the microbalance. Tests with an Ainsworth and a Kuhlman balance (*120*) showed that the drift of the zero reading was excessive under the conditions tested. An Ainsworth assay balance (*32*) was found to be less sensitive to temperature fluctuations than microbalances but more affected by vibrations. Microanalysis using a Mettler microanalytical balance has been discussed (*71*) and the present position of microbalances reviewed (*167*).

GENERAL AND REVIEWS

A discussion of the accuracy of organic microanalysis (*94*) indicates that the error is more often due to the method than to the analyst. General discussions have been published on the application of amperometric titrations (*141*), on errors in amperometric and starch-indicator methods (*23*), on ultramicromethods, apparatus, and techniques (*2, 47, 148*), and on recent developments in microanalysis (*92, 102*) and microapparatus (*76, 175*).

Reference materials or standards for all elements and groups commonly determined have been listed (*5*) and some new commercial products of interest to microchemists have been discussed (*16*). The work of two committees, one on the standardization of apparatus, the other on methods, was reviewed (*189*). Micromethods applicable to medicinal substances were described (*119*) and microanalysis and chemistry of specific, selective, and sensitive reactions were discussed (*48*).

A number of review articles concerning or related to organic microanalysis have been published during the past 2 years. Among them are an appraisal of microchemistry (*190*), a discussion of the progress and possibilities of organic microanalysis (*113*), a review of some new methods (*43*), a historical review of microchemistry (*53*), two general reviews on microchemistry (*3, 158*), and one on semimicrotechniques (*191*). Microanalytical methods for proteins in blood plasma (*151*) and for clinical analysis (*55*) have also been reviewed.

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Inorganic Microchemistry

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A TOTAL of 970 references have been considered in making up the present review. The limitation of space has necessitated discontinuing the former practice (*192*) of including an annotated bibliography. The references cited are not necessarily the most important individual contributions during the period under consideration; instead, they often typify important trends and illustrate points of significance in a critical appraisal. Many interesting papers have been omitted because they will appear in accompanying reviews of other fields.

Most of analytical chemistry is developing along lines that are essentially microchemical. To keep abreast of developments in microanalysis requires, therefore, consideration of the work in microscopy, fluorometry, x-ray diffraction and x-ray spectrometry, polarography, colorimetry, nucleonics, electrometric methods, mass spectrometry, emission spectroscopy, Raman and infrared spectroscopy, extraction methods, ion exchange, and chromatography. Obviously, reviews of other fields must be correlated with the present one to obtain a true perspective.

A general profile of the field of inorganic microchemistry can be obtained by a gross classification of the current literature. The present review, covering the 2-year period since October 1951, is based on a collection of almost a thousand references dealing generally with microchemical apparatus, separations, organic reagents, spot tests, microscopy, gravimetry, titrimetry, and colorimetry. Of these, 64 dealt with instruments and apparatus, and 151 were primarily contributions in the field of separations. It is interesting to note that 397 papers dealt with the application of organic reagents and very little attention was paid to inorganic reagents except where their utilization was incidental to the use of organic compounds. Spot tests appeared to be by far the most important qualitative technique, with a total of 93 references. Quantitative analyses described were very largely in the field of colorimetry, a total of 330 contributions falling in this category. There were 93 and 125 papers dealing with gravimetric and titrimetric methods, respectively.

This reviewer considers microanalysis to embrace all analytical operations dealing with small amounts of material (100 micrograms or less), regardless of dilution. Analysts in general prefer instruments or techniques that possess high sensitivities and the trend is toward operations applying to dilute systems.

Of special interest is the development of electrometric methods of great sensitivity. Coulometric titrations of exceptional delicacy are being reported in increasing numbers, and sensitive electrodeposition procedures are also proving significant. High-frequency titrations have proved useful for titrimetry of dilute solutions, especially in instances where satisfactory indicators or electrodes have not previously been available.

Specificity of reagents is still more of an aim than an actuality, and most instruments are restricted to measurements on isolated systems. Therefore, separations are an important factor in the progress of microchemical analysis. Of special interest in this connection is the great number of contributions dealing with ion exchange and inorganic chromatography that have appeared recently. The true value of this work can be assessed only through practical application. It is certain that many of the contributions have appeared because it is a new and intriguing field. In fact, some of the separations described can be accomplished in seconds rather than hours by using the same systems applied to solvent extraction methods rather than resorting to the use of paper or column chromatography. A number of difficult separations have been solved by chromatography or ion exchange, however, and work in these fields is contributing greatly to the furthering of inorganic microchemistry.

A passing observation of special interest to those in academic fields is the wide application of coordination chemistry in microanalysis. Over 60% of the papers reviewed dealt with some form of coordination, with applications ranging from masking of interferences by complexation through utilization of complexes as reagents or reacting substances.

The following sections will serve to show actual examples of trends and practices considered to be of special significance; attention is directed to accompanying reviews of related fields, and to critical reviews and theoretical discussions that have appeared elsewhere during the past two years.

REVIEWS

A number of phases of inorganic microchemistry have been reviewed by Furman (*59*). Singer (*161*) has dealt with microbalance techniques. Osborn (*135*) and Vermeulen and Hiester (*211*) have discussed analytical applications of ion exchange resins, and the theories and practices of solvent extraction methods have been surveyed by Sandell (*149*). The recent progress in automatic gravimetry has been discussed by Duval (*39*); Parks has reviewed the applications of amperometric titrations to microanalysis (*138*); and coulometric titrations have been evaluated by Tutundzic (*189*). The discussion of radiochemical techniques by Hudgens (*81*) presents a number of ideas of value to the microanalyst, and the summary by Haberlandt (*71*) of the use of luminescence in trace analysis is important. A brief but valuable review of micromethods for determining physical constants has been presented by Sobotka (*170*). The article by Bose (*19*) on the use of bioassay methods should be stimulating to those microanalysts not familiar with such techniques. A number of papers have appeared dealing with the question of reaction sensitivity and its designation—e.g., *72, 113*. This reviewer still favors the designations, "limit of identification" and "limiting concentration," in the forms originally proposed by Feigl and by Hahn. The use of the negative logarithm of the concentration as advocated by Wenger, Duckert, and Gillis does have value in the graphic indication of the effect of cosolutes on dilution limits.

APPARATUS

Balances of various types continue to be of interest, and Hodsman (*79*) has reviewed the factors influencing modern design. Singer (*161*) has reviewed the present status of microbalances and Bromund and Benedetti-Pichler (*24*) have discussed the use of the assay balance in microanalytical work. A glass microbalance has been described by Ambrosina (*9*) and various types of quartz fiber instruments have been discussed (*20, 28, 74*). An electronic balance was described by von Brockdorff and Kirsch (*23*) and a magnetically controlled quartz fiber balance was proposed by Edwards and Baldwin (*42*), who gave details of construction and performance data on their instrument.

The increasing interest in analysis on the microgram scale has resulted in a number of papers which deal with the special apparatus required for such work. El-Badry and Wilson (*45*) have discussed the apparatus and techniques involved in microgram analysis and Brindle and Wilson (*22*) described a micromanipulator for use with syringe micropipets. Alvarez Querol has also dealt with the problem of apparatus for ultramicroanalysis and has suggested various pieces of equipment of value for such work (*7, 8*).

Chromatographic and ion exchange methods generally require only the simplest of apparatus. However, certain innovations are of interest in these fields, as, for example, the instruments developed for automatic paper chromatography. Müller and Clegg (*129*) have developed a photometer for use in reading paper chromatograms. Incident light is reflected to a barrier layer photocell for reflectance studies or a modified instrument can be used for transmittancy measurements. Either developed chromatograms can be studied or continuous readings of chromatograms can be recorded during development. Rapid scanning of strips during separation should disclose peculiarities or other details of value in interpretation not available in completed chromatograms. Sato, Norris, and Strain (*151*) have developed an apparatus for continuous electrochromatography. The instrument serves to impress a potential of 200 to 500 volts across a paper strip carrying a solution of electrolytes to undergo separation. The actual technique employed is considered under the general discussion of separations.

A capillary buret has been described by Grunbaum and Kirk (*69*) suitable for conventional use or adaptable for use with a reagent-generating ion exchange column. In the latter use standard acid or base solutions are generated at the time of utilization by passing aqueous potassium chloride over an exchange column of Dowex 50 resin washed with hydrochloric acid or amberlite XE-67 previously washed with potassium hydroxide. A useful unit for paper chromatography capable of holding up to 50 strips at one time has been developed (*160*).

Liquid-liquid extractors of different types have been proposed. A special syringe extractor for use with solvents of low density has been suggested by Medalia and Stoenner (*121*) and a continuous extractor for high density solvents was discussed by Harman (*73*). Spence and Streeton proposed the use of a microrotary extractor (*171*), and Meinke and Anderson devised (*122*) a continuous extractor utilizing a nitrogen lift followed by a two-stage bubble extraction during the gravity return cycle.

The photomultiplier conversion of the Beckman DU spectrophotometer is of interest where an increase of sensitivity is desired (*32*). Opler and Miller (*134*) have also suggested modifications for the Beckman DU instrument to gain greater sensitivity and versatility.

An apparatus for microanalysis of gas samples was proposed by Madley and Strickland-Constable (*111*). The characteristics of porcelain microchemical apparatus have been studied by Whalley and Wyatt (*202*). A convenient micro drying oven has been devised (*153*) and micropipets have been described (*13, 154*). Flaschka has devised a reductor tube to be attached to a microburet so as to supply freshly reduced iron(II) or titanium(III) solutions (*57*). Lambert, Moore, and Arthur suggested a filtration apparatus for producing confined spots for spot test colorimetry (*102*). Various pieces of microchemical apparatus of simple construction have been pictured by Stock and Fill (*172*).

SEPARATIONS

Separations remain the heart of most analytical methods. The true meaning of this statement becomes clear upon noting that over 15% of all papers studied for this review dealt solely with such operations, and over 28% of the papers considered were found to contain relatively novel examples of isolation or separation. In studying the current literature it is impossible to overlook the rather sudden impact of chromatography and ion exchange. Of the papers on separations as such, over 75% were based on these two approaches.

It is to be expected that the number of the papers appearing in a relatively new area of investigation such as the chromatography of inorganic compounds would be of questionable value. Such is the case, but fortunately a substantial number of important contributions have also appeared, and a number of interesting trends can be noted.

Some unusual and difficult separations accomplished by paper chromatography include the separation and detection of various rare earths (*142*) through use of complex-forming 8-quinolinol in butanol solutions. Lederer proposed similar separations based on the use of acetylacetone as the complexing agent (*105*). Francium has been isolated in a radioactively pure state by means of a combination of ascending paper chromatography and chemical separations (*139*). Kember and Wells (*89*) described the separation of zirconium and hafnium; Lacourt, Sommereyns, and Soete proposed (*97*) a method of isolating uranium from iron and aluminum; and Lewis and Griffiths have developed a method of descending-liquid phase chromatographic separation of a number of metals (*107*). Lacourt and associates have applied paper chromatography to separations of anions on a microgram scale (*96*). Williams and his associates have used cellulose columns to separate tantalum from niobium (*26, 27, 207*). The fluoride complexes are chromatographed and final separation is then accomplished by eluting with methyl ethyl ketone–water or methyl ethyl ketone–hydrofluoric acid mixtures. Niobium and tantalum can also be separated as the oxalates on activated alumina (*185*).

The chromatographic separation of chelated compounds holds considerable promise (*77*). Al-Mahdi and Wilson (*6*) have studied the separation of certain metal-diethyldithiocarbamates, and a number of investigators have worked on the chromatography of metal complexes of 8-quinolinol (*77, 103, 147*). Cobalt can be isolated and determined by chromatographing the cobalt complexes of nitroso R salt (*34*) or 2-nitroso-1-naphthol (*12*). The reverse process of separation by complex elution is of proved value (*162*).

Electrochromatography has gained attention (*104, 106, 174, 175*). It consists essentially of electromigration combined with paper chromatography. Various combinations of cations and anions can be separated, and a considerable amount of flexibility in devising cation separations can be effected by use of complexing addenda whereby anion or cation complexes can be produced.

Ion exchange methods are becoming well established. An excellent application of such techniques is the isolation of trace materials. Various mixtures of materials that are ordinarily difficult to separate lend themselves to separation on ion exchange columns, particularly in combination with complex elution methods—for example, rare earths can be handled with relative advantage in this manner (*145, 146, 188*).

Extraction methods are rapidly gaining interest. Sandell has discussed the principles of the method (*149*). Selective extraction of lead iodide has been studied by West and Carlton (*194*), and a method for the isolation of copper has been reported (*200*). White and Rose reported a highly selective procedure for extracting antimony (*204*), rhenium has been extracted selectively as aryl phosphonium complexes (*186, 187*), and a study has been made of the extraction separation of chromium from vanadium (*25*).

Group separations by means of extraction techniques are of considerable importance. Gorbach and Pohl (*65, 66*) have recommended extraction with organic reagents as a means of concentrating traces of metals, and Abrahamczik (*1*) has presented a general discussion of various extraction methods. Bock has studied (*17*) the extraction of various metal thiocyanates, and Bock, Kusche, and Bock have separated metallic bromides by ether extraction (*18*). Miscellaneous extraction methods include: the separation of antimony (*197*); bismuth (*87, 201*); molybdenum (*118*); sodium and potassium (*203*); platinum (*41*); nickel (*64*); and iron, gallium, hafnium, indium, scandium, tellurium, uranium, vanadium, and zirconium (*56*).

Gathering agents mentioned as collectors for trace metals include hydrated iron oxide for beryllium (*98, 99*) and tellurium for silver (*150*). Electrographic separations are elegant (*30*) and electrodeposition finds use for separation even in the microgram range (*5*).

Strictly speaking, complexation is not a means of separation in most cases. It does serve the same purpose, however, and masking interferences by adding complexing agents is an extremely useful technique. For example, germanium can be determined in the presence of many potential interferences by the expedient of adding oxalic acid (*130*). Iron and aluminum interferences in the determination of beryllium have been obviated by means of ethylenediaminetetraacetic acid (*2*). Germanium has been sequestered as the fluoride complex (*21*) and ethylenediaminetetraacetic acid complexes of lanthanons (*191*) have been used in accomplishing their separation. This latter example serves to illustrate the actual physical separation of materials by means of complexation. The lanthanon complexes are selectively released by fractional acidification so as to produce individual separations.

QUALITATIVE TECHNIQUES

Spot test methods make up the bulk of references dealing with qualitative analysis. Feigl (*49*) has reviewed the chemistry of specific, selective, and sensitive reactions and West has discussed the methods utilized in developing spot tests (*193*). West and Hamilton have shown that the characteristics of spot tests are greatly dependent on the nature of the reaction medium (*198*). Various spot tests for use in identifying alloys have been summarized by Wilshaw (*208*), and Monk has reviewed (*128*) the development of electrographic analysis.

Individual contributions of special interest include the hydrazine test described by Feigl and Mannheimer (*52*). As little as 0.001γ of hydrazine on spot test paper gives a red color with *p*-dimethylaminobenzaldehyde. When the test is run on paper, a salmon-pink fluorescence is obtained; when the test is performed on the spot plate, no fluorescence can be noted and even the normal test color is changed (yellow instead of red). A very sensitive test for copper, using Alizarin blue, has been proposed by Feigl and Caldas (*50*), and Feigl and Heisig have utilized "lake" formation as the basis for test for palladium and cyanide (*51*). A general test for the rare earth elements, based on the use of *o*-arsenobenzeneazo-2′,1′,8′-dihydroxynaphthalene-3′,6′-disulfonic acid, has been described by Kuznetsov (*95*). Pizarro has studied the use of gossypol as a reagent for detecting tin(IV) (*140*) and molybdenum(VI) (*141*). Benzhydroxamic acid is capable of detecting as little as 0.005γ of vanadium (*33*); diphenyl phosphate has been recommended as a reagent for the detection of bismuth, iron, aluminum, and titanium; and the 1-methyl-2-mercaptoglyoxaline–bismuth complex has been suggested as a reagent for the detection of iodides (*109*). A new spot test for zinc has been described by Belcher, Nutten, and Stephen (*14*); and West and Longacre have proposed a catalytic test for cobalt (*199*). The fluorescence test for lead described by Slijivic (*163*) is of significance.

A few new microscopical tests have been proposed. The microscopical distinction of zirconium and hafnium has been described by van Nieuwenburg and van Ligten (*132*) and the formation of thallium thiocarbamide perchlorate crystals is suggested (*112*) as a test for thallium. West and Granatelli have shown that chromium(III) can be detected as the phosphate (*196*) and Ryan, Yanowski, and Cefola (*148*) have suggested trioxalato complex formation as a general test for iron, aluminum, chromium, and cobalt. An innovation in microscopical procedure is the fusion technique described by West and Granatelli (*195*), whereby inorganic salts are fused with 8-quinolinol on the hot stage and the resulting chelates and acid salts of 8-quinolinol serve for the simultaneous identification of both cations and anions. The use of the ultraviolet microscope is interesting and the work of Stolyarov (*173*) in this field should be consulted. Polarized light microscopy deserves far more attention than it is now being given (*15*).

Applications of the classical schemes of qualitative analysis to microchemical methods have been of restricted interest, except for the work of Wilson and his associates in developing methods for ultramicrochemical analysis (*43, 46, 47*).

Infrared spectra serve for the analysis of inorganic compounds, and the salts of polyatomic ions can often be identified (*124*) by noting the positions and intensities of the *IR* absorption bands.

GRAVIMETRY

The work of Duval and his associates constitutes the most significant development in gravimetric methods of microanalysis. By means of thermogravimetric techniques, this group of investigators has studied practically all of the precipitates used in the gravimetric determination of the various cations and anions. The data obtained show the optimum temperature ranges for drying or igniting precipitates and disclose a number of erroneous procedures that have been in use in which specified directions for the treatment of precipitates yield impure or unstable weighing forms. The thermogravimetric technique itself holds promise as an automatic microanalytical tool. The many contributions in this field have been summarized by Duval (*39*) and his book on the subject (*40*) presents a complete description of the instruments and techniques utilized as well as the data obtained to date on the precipitate studies.

Very significant developments have taken place in the analysis of microgram amounts of sample. Balances and other equipment for such work were discussed under the section devoted to apparatus. Gravimetric procedures for lead, silver, and mercury(II) have been presented by El-Badry and Wilson (*44*). These same authors have proposed (*48*) a semiquantitative procedure for vanadium on the microgram scale based on the precipitation of lead vanadate, with subsequent centrifugation and estimation of the volume of the precipitate.

A number of new precipitants have been proposed and renewed interest has been shown in some of the old ones. Tetraphenylboron has gained a great deal of attention, and numerous papers dealing with it have appeared. It is of special interest because it is a selective precipitant for ammonium, potassium, cesium, rubidium, and calcium (*210*). It is claimed to be specific for potassium and ammonium when precipitations are performed in 0.1N mineral acid (*91*). In addition to the interest in special precipitants, interest should be centered also on conditioning agents used to increase the selectivity of reagents. For example, Pribil has shown (*144*) that 8-quinolinol becomes a selective reagent for iron, aluminum, magnesium, and uranyl ions when ethylenediaminetetraacetate is used as a "masking" agent in ammoniacal solution. Likewise, ammonia will only precipitate beryllium, zirconium, and titanium from "complexone" solutions. Milner and Wood have been able to determine tantalum as tantalum pentoxide (*125*) by isolating the fluoride complex by means of a methyl ethyl ketone extraction. The extracted tantalum is precipitated as the tannate.

TITRIMETRY

The use of ion exchange resins in the preparation of very dilute standard acids and bases is of considerable interest. Kirk and his collaborators have shown (*69, 70*) that standard potassium hydroxide (~0.0010N) can be prepared by passing standard potassium chloride through a column of Amberlite XE-67 resin that has been first treated with sodium hydroxide and then washed until the effluent is neutral. Once the column has been prepared and set in operation, fresh standard base can be drawn off as needed. The authors found that for 45 titrations, over a 45-day period, titrations against a standard acid gave a standard deviation of ±0.171 μl. for an average titration of 43.34 μl. Standard hydrochloric acid can be generated in a similar manner by using an acid treated Dowex 50 resin.

Delavault and Irish (*35*) have proposed the use of direct titrations of metals by means of dithizone. They recommend the use of 80% acetone in water as the solvent, since stable emulsions are formed with carbon tetrachloride solutions of the reagent. Air oxidation of the reagent can be suppressed by adding phenylhydrazine sulfate to the solution to be titrated. Microtitrations of metals can be performed using ethylenediaminetetraacetic acid (*58, 155*). This titrant should also be well adapted to use with high-frequency oscillators which hold promise for microchemical work on the basis of their sensitivity and because they obviate difficulties often associated with electrodes of potentiometric or conductometric titrators. In general, high frequency methods hold greatest promise where lack of suitable indicators or electrode systems has restricted the use of titrimetry as, for example, in the case of the titrimetric determinations of thorium (*16*) and sulfate (*126*).

Coulometric titrations hold great promise in microanalysis. Modern electrometer tubes can measure extremely small currents and potentiometric indication of end points now makes it possible to work with relative ease in the submicrogram range. Examples of such titrations include the coulometric determination of manganese by Cooke, Reilley, and Furman (*32*); acids by Carson and Ko (*29*); silver by Lord, O'Neill, and Rogers (*108*); uranium by Furman, Bricker, and Dilts (*60, 61*); and vanadium by Furman, Reilley, and Cooke (*63*). These latter investigators have also pointed out the merits of the coulometric method in cerate titrimetry (*62*).

Amperometric titrations hold promise in microanalysis, particularly when used with some of the organic titrants (*85*).

COLORIMETRY AND SPECTROPHOTOMETRY

Techniques and reagents both hold interest in this area. Kirk and his associates have shown how even submicrogram quantities of phosphate can be isolated and then determined using capillary cells in a Beckman DU spectrophotometer (*152*). A relatively new area of activity is the ultraviolet spectrophotometry of inorganic compounds (*10*). Working in the ultraviolet range, Telep and Boltz have determined vanadium (*181*), columbium (*182*), and cobalt (*183*). Hines and Boltz suggest determining titanium with ascorbic acid (*78*), measuring the absorbency at 360 mμ. Rogers and his associates suggest determining iron (*37*) as well as bismuth, lead, and thallium by ultraviolet spectrophotometry (*123*). Higginson also used this general approach for estimating mercury(II) (*76*).

An interesting area of colorimetric analysis is radiation dosimetry. One such method for measuring radiation depends on estimating the amount of acid liberated from chloroform in the presence of water, using bromocresol purple as the indicator (*178*). Polson and Strickland (*143*) have collected traces of sulfate on barium chromate and determined the sulfur through formation of Lauth's violet. Martin and McClelland determined cyanate as the dicyanatopyridine copper(II) complex (*119*). Miscellaneous colorimetric methods of interest include the determinations of millimicrogram amounts of zinc (*117*), gallium (*127*), thorium (*120*), and zirconium (*133, 184*).

Yoe and his associates have proposed important new colorimetric reagents for zinc (*211*) and molybdenum (*212*) and Smith with his collaborators have developed new reagents for copper (*110, 168, 169*) and iron(II) (*205*). Murexide is being used for colorimetric calcium determinations (*136–138*). Ferguson and Banks have studied various dioximes and recommend cyclohexane-1,2-dionedioxime for determining nickel in calcium (*54*): They also report that 1,2-cycloheptanedionedioxime provides sensitivity advantages for spectrophotometric determinations of nickel (*55*). Uhlig and Freiser (*190*) have proposed the use of 2-isothioureidopropionic acid as a color-developing agent for nickel.

ORGANIC REAGENTS

Organic reagents are of utmost importance in the development of inorganic microanalysis; in gravimetry, titrimetry, colorimetry, spot tests, and even in the field of separations, the majority of agents used are organic compounds. All of the organic reagents encountered cannot be mentioned, and it is even impractical to try to discuss new compounds that have been introduced. It is pertinent, however, to call attention to the discussion of the selectivity of organic reagents by Irving and Williams (*84*) and the remarks of Kuznetsov concerning the bases of color reactions of organic reagents (*94*). The new reagents developed in the laboratories of Yoe (*211, 212*) and Smith (*110, 168, 169, 205*) illustrate the benefits to be derived from systematic research in this field. Other studies worthy of mention are those of Tchakirian and Bavillard on new reagents for germanium (*179, 180*), Malissa and Miller on disubstituted dithiocarbamates (*114*), Korenman and Sheyanova on reagents for boric acid (*92*), and Kantharaj Urs and Neelakantam on pentamethylquercetin as a reagent for boric acid (*88*). An interesting side light appears in the paper of Feigl and Schaeffer (*53*), which deals with the difficult problem of decomposing metallo-organic complexes. They recommend the use of persulfate oxidation, catalyzed by traces of silver ion.

MISCELLANEOUS

Analysis by radioactivation promises to be an extremely valuable tool for microanalysis. Because of limitations imposed by the need for sources of radiation, the method is restricted to work done in special laboratories and for this reason is not emphasized here. The review on the subject by Smales should be consulted (*165*). Representative analyses by radioactivation include the determination of uranium (*164*), arsenic (*166, 167*), sodium and copper (*3*), thallium (*36*), antimony (*82*), indium (*83*), and various traces impurities in magnesium (*11*).

Catalyzed and induced reactions are often ideally suited for qualitative and quantitative microanalysis. A number of contributions appeared in this field recently, including the work of Szabo and his associates on the determination of persulfate (*176*) and Krause's work on the estimation of iron (*93*). This latter method is reported capable of disclosing as little as 0.0001γ of iron, and is based on the catalysis of hydrogen peroxide decomposition by iron(II) hydroxide coprecipitated on copper and cobalt hydroxides. A major proportion of research on catalytic methods has been carried out in Japanese laboratories. Shiokawa has studied methods for determining osmium (*156, 157*), vanadium (*158*), and molybdenum (*159*). Goto and Suzutu have evolved catalytic methods for estimating copper (*67*), and the determination of iodide has been studied by Iwasaki, Utsumi, and Ozawa (*86*). Catalytic methods have been described for determining copper (*100*) and fluoride (*101*). The iodine-ozide reaction has been used by Holter and Lovtrup for the determination of various sulfur compounds (*80*). A catalytic test for cobalt has been proposed by West and Longacre (*199*).

Bioassay methods are being generally overlooked, in spite of the fact that they can offer sensitivities beyond those obtainable with chemical methods and may exhibit considerable selectivity. Nicholas has discussed the use of *Aspergillus niger* and *Penicillium glaucum* in estimating trace metals (*131*). Copper in soils in quantities up to 1γ can be estimated by means of *Aspergillus niger* (*38*) and this same organism can be used for molybdenum determinations (*75*).

The value and scope of fluorometric methods can be seen in the papers of Zocher, Feigl, and Torok on the fluorescence of metal salts of 8-quinolinol (*213*); Willard and Horton on the determination of fluoride (*206*); and Alford, Shapiro, and White on the determination of zirconium (*4*). Fluorescence is valuable in both qualitative and quantitative analysis and often exhibits unusually good sensitivity and selectivity.

Gas analysis on the micro scale has attracted a limited amount of attention. Wirth (*209*) has described an application of the heat conductivity principle to the analysis of gas samples of from 1 to 0.001 ml. The samples are absorbed in a U-tube packed with activated charcoal and partially immersed in liquid air. The gas is desorbed by controlled evaporation of the coolant and its heat conductivity measured in special cell. Colorimetric analysis of air for industrial vapors and gases has been discussed by Grosskopf (*68*). Malissa, Musil, and Kreibich have investigated various methods of identifying volatilized inorganic substances (*115, 116*).

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Fluorometric Analysis

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THIS review on fluorometric analysis covers the 2-year period from approximately October 1951 to October 1953, and is a continuation of similar previous surveys (*182*).

BOOKS AND GENERAL ARTICLES

A new edition of Radley and Grant's book "Fluorescence, Analysis in Ultraviolet Light" (*144*) is now in the final stage of publication and is scheduled to be available the latter part of December 1953. Danckwortt (*27*) has published the fifth edition of his book dealing with analysis in ultraviolet light; however, this is not a revision and is identical with the fourth edition. The author states in his preface that the new edition was published in demand for copies of the book, and because of the difficulty in obtaining foreign publications during the war a revision was not possible. Bowen and Wokes (*14*) have published a book dealing with the fluorescence of solutions which is designed for practical workers and beginners in the field of fluorescence. Brief discussions of light absorption, the theory involved in fluorescence and fluorescence quenching, and a description of fluorometers are included. This book should be received as a welcome addition to the literature on fluorescence. A book by Garlick (*58*) deals with the general subject of luminescent materials and includes a discussion of fluorescence as well as thermoluminescence and phosphorescence. Most of the book is devoted to the subject of phosphors. One section deals with the fluorescence of organic substances and the author discusses quenching, polarization, etc.

A chapter on fluorometric analysis is included in a text on instrumental analysis (*11*). This book is written by specialists in each of ten fields of analysis and is designed for university seniors or graduate students; however, the experienced analyst will find many helpful suggestions. Directions are given for constructing the equipment necessary for the fluorescence laboratory; filter selection, standard, etc., are discussed. A chapter on fluorescent indicators with 54 references is included in a book (*17*) on analytical methods published in Germany. Koller (*101*), in a book called "Ultraviolet Radiation," covers a subject of interest in exciting fluorescence. The author discusses types and sources of radiant energy. Many charts and tables are included to give the characteristics of various arcs, lamps, glasses, and reflectors. Indemans (*82, 83*) has published the results of his rather extensive study of factors concerned in the measurement of fluorescence in quantitative determinations. This author presents a theoretical treatment of absorption of the exciting light and the relation of the emission to concentration is considered in connection with the Beer-Lambert-Bougier law as modified for fluorescence. Formulas are given to show the quantitative action of quenching agents. A chapter on inorganic fluorescence analysis is included in the report (*112*) of the national conference on air pollution Bowen (*13*) has given a discussion of the mechanism of luminescence of organic substances and considered the application of these materials to scintillation counters. Radley (*143*) has reviewed the application of fluorescence in agriculture, food, leather, paint, rubber, medical, mining, and engineering industries. The less common analytical methods based on fluorescence are reviewed by Deribere (*31*). A round-table discussion on fluorometric analysis was held by the Division of Analytical Chemistry at the Buffalo meeting (*183*). Topics discussed included uranium analysis, geochemical applications, and analysis of biological and organic materials.

The general aspects of fluorometric determinations is the subject of an excellent paper by Braunsberg and Osborn (*16*). The mathematical considerations of previous authors have been extended and consideration is given to the effect of the exciting source, impurities, quenching, etc.

The application of ultraviolet light to absorption analysis including the transmitted, reflected, or fluorescent light resulting therefrom is discussed by Brumberg and Gershgorin (*20*). These authors give a description of methods and apparatus applied to paper chromatography of colorless substances under visual or photographic observation. Lauer (*106*) in a study of light absorption and fluorescence has developed an expression for the total fluorescence observed in terms of the absorption coefficient. A general article on luminescent materials by Ward (*178*) provides interesting background material for anyone working in fluorescence.

APPARATUS

Some analysts have found confusion in ordering high pressure mercury vapor lamps since the General Electric Co. has changed its designation on these lamps. The changes in numbers on the lamps in most common use are as follows: AH4 to H100A4, BH4 to H100BL4, CH4 to H100SP4, EH4 to H100FL4; the suffix H indicates a mercury vapor lamp, 100 is the wattage, and the final number indicates the type of ballast required. A description of these ultraviolet sources and their spectral characteristics is given in a new 8-page folder (*59*). The new xenon arc lamp (*3*) may be useful for research and other particular applications as a source of ultraviolet radiation. This lamp gives an intense, practically continuous spectrum from 2000 to 7500 A.

An effective modification of the Beckman spectrophotometer has been devised by Huke and his associates (*79*) for the measurement of weak fluorescence spectra. In this instrument the cuvett compartment is redesigned so that ultraviolet-exciting radiation enters the top of the cuvette, and the fluorescent light passes through the slit and traverses the prism in the reverse direction and emerges at the usual entrance of the light source, where it is brought in contact with a 1P28 electron multiplier tube. Musha (*121*) has designed a simple electrophotometer using a selenium photocell and has applied it to fluorescence titrations. Haines and Drake (*71*) have described a fluorometer for scanning fluorescent paper chromatograms. A simple apparatus for measuring the fluorescence on filter paper strips in which the paper is placed between the exciting source and the photocell is described by Semm and Fried (*156*). An arrangement for allowing ready observation of the change of end point of fluorescent indicators and providing for the convenient reading of burets has been devised by Deibner (*29*). Several attachments have been designed for making particular types of fluorescence measurements with the Beckman spectrophotometer. One of these (*107*) is designed to measure the fluorescent spectra of highly absorbing oils and another (*32*) is made especially for measuring the spectral reflectance characteristics of fluorescent materials.

Simplified techniques including the lamp reflector, filters, etc., for use in fluorescence microscopy have been described by King (*97*). Attachments have been devised to adapt the General Electric spectrophotometer for the detection and measurement of fluorescence (*9, 174*). Fletcher and Warner (*47*) have developed a versatile fluorometer for the measurement of the fluorescence of solutions. The fluorescent light is measured by a 1P21 electron multiplier phototube and a microammeter.

Schwartz and his associates (*155*) have described a modification of the Farrand fluorometer which is extremely sensitive. A simple fluorometer using an RCA 931A electron multiplier phototube has been built by Germek (*60*) and his associates for measuring the fluorescence of proporphyrins.

Fluorometers which have been developed essentially for uranium analysis at the U. S. Geological Survey are described with construction details in a recent bulletin (*67*). This publication contains much information that will be welcomed by anyone attempting to construct a fluorometer.

A patent has been issued (*173*) for an apparatus for observing fluorescence, which consists essentially of a black box, an exciting source, and a spectroscope.

Phillips Scientific Corp. advertises a new model of its chromatographic analyzer which is designed to facilitate observation of absorption columns under ultraviolet light (*137*).

A simple home made fluorometer for use with test tubes has been designed by McGillvray (*114*). This fluorometer employs a Weston photocell attached to a galvanometer.

A device for the automatic recording of the fluoride content of the air appears to be a very important addition to fluorometric apparatus (*25*). In this apparatus a tape impregnated with magnesium-8-quinolinol is pulled through a sampling area and thence between an ultraviolet source and a photocell. Suitable filters remove all undesired light and a recorder is attached to the photocell.

INORGANIC APPLICATIONS

An interesting technique reported in a previous review in which a fluorescent screen is employed to detect a colorless object absorbing in the ultraviolet has been applied by Stolyarov (*165*) to the detection of several inorganic ions. The material under observation is placed on a microscope slide and illuminated from underneath with a colored ray of light and ultraviolet rays. The rays are projected through the microscope on to a screen which fluoresces white under the action of ultraviolet rays. The object which transmits the colored ray and absorbs the ultraviolet appears colored on a white background. The author describes the use of this method in the detection of ammonium, potassium, sodium, iron, and cadmium ions after precipitation with various reagents.

Indicators. Fluorescent indicators for acid-base reactions is the subject of a review by DeMent (*30*). About 60 such indicators are listed with their pH change values. A general study of fluorescent indicators is reported by Tomicek and Suk (*172*). These authors review this field with 104 references and give results on a number of new indicators. Podall (*138*) believes that 5,7-dihydroxycoumarin gives an end-point change from pH 5.5 to 5.8 that is more easily observed than the phenolphthalein color change in titrations.

Goto and his associates (*66*) are making an extensive study of the use of fluorescent indicators in oxidation-reduction titrations. These workers have shown that rivanol, phosphine, harmine, and tripaflavin serve as good indicators for titrations with oxidizing agents such as permanganate, hypochlorite, iodine, and bromine. The titration of sodium chloride with silver nitrate using fluorescein as an indicator has been studied (*121*) with the use of a photoelectric fluorometer. A sharp change in fluorescence occurs at the end point and the previous work of Goto using fluorescein and eosin as indicators in titrations of this sort have been confirmed. The 8-quinolinol complexes with the metal ions have been the subject of a number of articles. Feigl and his associates (*43*, *44*), have shown that these complexes will form in fused mixtures, nonaqueous solutions, and vapors, as well as in the usual water solutions. The formation of the fluorescent complexes when 8-quinolinol is dropped on filter paper serves to show the presence of aluminum, calcium, or magnesium and will differentiate qualitative from quantitative filter papers.

The application of 8-quinolinol-impregnated papers to the separation of the inorganic cations has been studied by Laskowski and McCrone (*105*). The R_f values were determined in several solvents. It was found difficult to distinguish lead, calcium, and barium bands under visible light, but these were easily defined under ultraviolet light. Reeves and Crumpler (*146*) have studied the chromatographic separation of the 8-quinolinol complexes of a number of common metal ions by forming the complexes in buffered acetic acid and then carrying out the separation with developing solvents. Observations are recorded for both daylight and ultraviolet light. The conditions for the separation of the metal–8-quinolinol complexes from chloroform solution by absorption on silica columns and eluting with chloroform have been determined by Hilliard and Freiser (*76*). The solutions of the complex with aluminum, gallium, indium, and zinc are easily distinguished by their fluorescence.

8-Hydroxyquinaldine seems to offer some promise as an analytical reagent (*136*). Fluorescent solutions are produced when zinc, cadmium, and aluminum salts are added to molten 8-hydroxyquinaldine at 100° C.; and lanthanum, gallium, indium, and scandium give yellow fluorescent precipitates from water solutions. The thorium complex with this reagent precipitates from acetic acid solution upon the addition of aqueous ammonia.

The paper chromatography of the cations with six different substituted 8-quinolinols has been studied by Fernando and Phillips (*45*). In several cases distinct differences from the normal 8-quinolinol were noted. For example, 2-methyl-8-quinolinol does not give a precipitate with aluminum in water solution but does form a fluorescent spot on filter paper.

Kakita and Goto (*87*) have used cochineal and rhodamine B as well as 8-quinolinol as fluorescence reagents in paper chromatography experiments with the cations. These workers used the techniques of brushing on the reagents after drying the chromatograms and also soaking the papers in the reagent before immersing in solutions of the metallic ions. The fluorometric microdetermination of sodium seems to be very successful using the paper chromatographic technique with zinc uranyl acetate as a developing agent (*169*).

Fluoride. Willard and Horton (*185*) have made an extensive study of fluorometric reagents for the analysis of fluorides. Excellent results for micro quantities of fluoride were obtained with the aluminum-morin reaction in alcohol and aluminum with 8-quinolinol. The aluminum-morin reaction for the determination of fluoride has also been used by Spence and his associates (*164*). The method that seems to be the most promising for the determination of micro quantities of fluoride has been described by Powell and Saylor (*139*). These authors found the aluminum complexes with Superchrome Garnet Y and Eriochrome Red B most suitable for this determination. The former is the better reagent and gives a very intense yellow fluorescence with aluminum. Standard solutions are made with the aluminum dye complex and the decrease in fluorescence on the addition of fluoride is measured. Phosphate does not seriously interfere. The range of 0.2 to 100γ of fluoride is covered with considerable accuracy.

The monitoring of the fluoride concentration in the atmosphere has been accomplished with the magnesium–8-quinolinol complex in a continuous recorder (*24*, *25*).

Uranium. The current interest in the discovery of new sources of uranium has necessitated the analysis of uranium in a wide variety of materials. The fluorometric methods and apparatus in current use at the U. S. Geological Survey are described in a booklet (*67*) which may be obtained from the survey. A review of the chemical methods for the determination of uranium has also been given by Rabbitts (*142*). This subject has also been reviewed by Price *et al.* (*140*) and Zimmerman (*193*). A series of articles on the determination of uranium has been published by Nakanishi (*124*, *125*). The methods of uranium analysis used in Belgrade are described by Draganic (*35*). A general study of this subject has been made by Jacobs (*84*). An investigation on the determination of uranium in phosphoric acid has been conducted by Yeaman (*191*). For the isolation of micro quantities of uranium from biological material Glover (*62*) recommends precipitation of uranium with protein as a uranium-protein complex prior to the fluorometric determination. The fluorescence of uranium in concentrated sulfuric acid may be used for its determination (*187*). Analysts using the fluorescence of uranium salts measured through narrow band filters will be interested in the article by Sevchenko *et al.* (*158*) in which are reported the fluorescent spectra of the various hydrates of uranyl nitrates. There is considerable variation between the hydrates and it appears that the previously published data correspond chiefly to the monohydrate.

Aluminum. The reagent Pontachrome Blue Black R has been found successful for the direct determination of aluminum in sea water (*119*) and in beryllium (*37*). In the latter case iron is removed by extraction with methyl ethyl ketone. The fluorometric determination of aluminum with the chloroform extract of the 8-quinolinol complex is the subject of an 11-page bulletin by Zimmerman (*194*). The application of this method to the determination of aluminum in bronzes shows excellent results (*65*). Aluminum can be determined in copper-base alloys without the removal of iron by titration with fluoride when morin is used as a fluorescent indicator (*98*).

Beryllium. The use of morin for the determination of beryllium has been the subject of many papers mentioned in previous surveys. An intensive study of this method for beryllium has been reported by Laitinen and Kivalo (*104*). The high purity morin necessary for this determination can now be obtained from several commercial sources. Additional reports on the beryllium-morin reaction have been made by Blair (*10*) and Welford and Harley (*181*). The determination of beryllium in ores with the fluorometric reagent 1,4-dihydroxyanthraquinone is finding successful application in India (*12*).

Rare Earths. The possibility of using the fluorescence of solutions of the rare earths for analytical purposes is being investigated by Huke and his associates (*79*). Variations in the fluorescent spectra of these solutions seem to offer some possibilities in this respect. The previously reported fluorescence of samarium and gadolinum in borax has been shown by Zaidel and Malakhova (*192*) to be due to other rare earths. Fluorescence in the rare earth minerals according to Haberlandt (*70*) is enhanced by lead and decreased by the presence of iron. The results of analytical studies on the fluorescence of samarium in calcium tungstate and sulfate have been reported by Peattie and Rogers (*133*).

Minerals. The effects of heating, cooling, crushing, etc., on the fluorescence of minerals have been studied by McDougall (*113*). Mackay (*115*) has reported on the determination of columbite by ultraviolet light. While fluorescence x-ray analysis is not included in this review it should be noted in connection with the mention of columbite that x-ray fluorescence seems to have solved the difficult problem of analysis of minerals for niobium and tantalum. A paper (*21*) describing the determination of niobium and tantalum was part of a symposium on the application of x-ray fluorescence analysis. Review papers on this technique also were presented at the symposium (*7, 51, 127*). Ultraviolet light inspection of samples of sillimanite has been shown to be an important application of fluorescence (*48*); kyanite seems to be the only sillimanite mineral that shows a fluorescence.

Miscellaneous Elements. The use of zinc and cadmium sulfides and silicates as fluorescent tracers of atmospheric dusts has distinct advantages over many other materials (*135*). These phosphors are easily identified as single particles. They are inexpensive and do not normally occur in the atmosphere.

Lead can be detected in amounts as low as 0.1γ by the fluorescence of the lead iodide–cadmium iodide precipitate which is produced in water solution (*162*). A new fluorescent reagent for tin has been discovered by Anderson and Garnett (*2*). The reagent is the ammonium salt of 6-nitro-2-naphthylamine-8-sulfonic acid and it produces an intense blue fluorescence with as little as 1γ of stannous tin. Propylthiouracil serves to detect 0.1γ of copper as a red fluorescent spot on a glass slide (*92*).

Thiamin has been reported by Wachsmuth (*177*) to produce an extremely delicate test for zinc, phosphate, and silicate. The sensitivity for zinc is one part in 10^6, for phosphate 0.25 part in 10^8, and for silica 0.2 part in 10^7.

Since chemiluminescence and fluorescence come under the same general classification, it is thought appropriate to mention here the application of siloxene as an *oxidation* luminescent indicator (*94, 95*) and as an indicator for the titration of lead with chromate (*96*). Lucigenin is recommended (*40*) as an acid-base luminescent indicator. One advantage in these luminescent indicators is the ease of detection of the end point with a photoelectric cell.

BIOLOGICAL APPLICATIONS

An article by Schulz *et al.* (*154*) on experiences with fluorescence in the analysis of milk and dairy industry products describes a number of interesting applications of fluorescence analysis. For example, the activity of bacterial cultures containing riboflavin reductive systems can easily be followed and the degree to which milk has been heated is indicated by the riboflavin destroyed. The general application of fluorescence to research in medicine is discussed by Rosental (*148*). Niccolini (*126*) has written a general article on the use of fluorescence analysis in biology and pharmacology.

The application of the fluorescence microscopy has been the subject of a number of papers—for example, the use of fluorescent dyes in staining bacteria (*6, 36*), the application of the fluorescent microscope to fundamental biological investigations (*117, 167*), the determination of atabrins deposited in the membranes (*93*), and the tracing of carcinogenic hydrocarbons in the skin and stomach wall of mice (*128*). A very instructive booklet giving many directions for the fluorescence microscopy of biological materials may be obtained from the New York representative of the Reichert Optical Co. (*147*).

For the determination of fluorescein passing through capillaries of a rabbit's ear Lichter and Schiller (*110*) place a photomultiplier tube over the ocular of a microscope and examine the ear under illumination with ultraviolet light. The investigations of Ilina (*81*) on fluorescence methods in the determination of carcinogenic products which were mentioned in a previous review have been continued and the fluorescent spectra of these materials at the temperature of liquid air have been determined.

The fluorometric determination of the estrogens has been investigated by Braunsberg (*15*) and he has recorded his results on the comparison of five methods in an excellent article. Other informative experiments on this determination have been published by a number of authors (*46, 63, 163*). The fluorescence spectra, the absorption spectra, and the relation of exciting wave length to fluorescence intensity of estrone, estradiol, and estriol are reported by Aitken and Preedy (*1*). These authors show that the order of decreasing efficiency of the exciting wave length was as follows; 4358, 3650, 4678, 4047, 4800, 5086 A. The first two of these are satisfactory for exciting the fluorescence. Strickler and his associates (*166*) in a paper at the Pittsburgh analytical conference reported on their experiments on the analysis of steroids in urine. The successful application of the fluorometric method of determining estrogens in urine are also recorded by others (*5, 73, 176*).

An apparatus for examining paper chromatograms of steroids has been described by Haines and Drake (*71*). The method of observation is based on the high absorptive properties of the steroids for short-wave ultraviolet radiation in the vicinity of 2500 A. A short-wave, 8-watt germicidal lamp is placed in the bottom of a small box. A glass plate covered with a zinc silicate phosphor is placed on top of the box with the phosphor on the underside. The papergram to be examined is placed between the lamp and the phosphor. The steroids appear as dark spots against the green fluorescence of the phosphor. This method has been successfully applied by Shull and others (*161*).

A study of the transformation of adrenaline, noradrenaline, adrenalone, and noradrenalone to fluorescent compounds shows that of these compounds only adrenaline will produce a fluorescence under the selected conditions and its fluorescence is greater if oxidized in acid rather than in sodium acetate solution (*131*). A comparison of the fluorometric to the biological method of determining adrenaline in venous blood showed that the two varied considerably but the noradrenaline values were about the same by both methods (*19*). The effect of pH on the fluorescence of adrenaline and its analogs have been studied by Supek (*168*). Directions for the separation and fluorometric determination of adrenalinelike substances are given by several authors (*108, 116, 153*). Tyrosinase has been shown by Mylon and Roston (*122*) to serve as a catalyst for the oxidation of adrenaline and increases the effectiveness of the fluorescent method for the determination of catechols. A method for the detection of some precursors of adrenaline by paper chromatography has been described by Shepherd and West (*159*).

An excellent paper has been published by Schwartz and his associates (*155*) on an improved method for the determination of urinary coproporphyrin. This article describes critical tests of the factors involved in this analysis, fluorometric standards, filters, the excitation wave length, and a modified fluorometer using a 1P21 photomultiplier tube. Concentrations from 0 to 5γ of the coproporphyrin per 100 ml. gave a straight-line relationship with fluorometer readings. This analysis for coproporphyrins and the construction of a fluorometer using a 931-A. photomultiplier tube is also described by Germek (*60*). Weber and Ruzdic (*180*) claim that the fluorescence of porphyrins is much stronger in sulfuric acid than in hydrochloric acid solution and recommend that the ether extract be shaken with 10% sulfuric acid. Fukumura and Fujisawa (*56*) have suggested a method for the determination of urinary coproporphyrins based on the color of the fluorescence at various concentrations. The quenching of the fluorescence of porphyrins and of chlorophyll has been studied by Livingston *et al.* (*111*) and this article should be of importance to those interested in the analysis of these substances.

Since a recent book on vitamin methods by Gyorgy (*68*) covers much of the literature on this subject, only a limited number of references are given here. Gyorgy's work is in two volumes. Volume I is devoted to chemical, physical, and microbiological methods of analysis for the vitamins and contains a general discussion of fluorometric methods including the fluorescence microscope method for vitamin A in tissues. The appendix of this volume has a section covering commercial fluorometers. Volume II (*69*) of "Vitamin Methods" consists mainly of animal and biological assays but also includes supplementary material on the physical, chemical, and microbiological methods of volume I. Chemical methods for the analysis of vitamins were reviewed at the eleventh International Congress meeting in London (*72*) and at a meeting of industries in Brussels (*23*).

Aoyama and Fujita (*4, 53, 54*) have improved the method of determination of vitamin A by chromatographic separations and by saponification of the fatty acid residues.

In the determination of riboflavin with the Pfaltz and Bauer fluorometer a correction for the nonlinear response has been suggested by David and Libbey (*28*) so that correct concentration values can be readily obtained. The microdetermination of riboflavin and flavin nucleotides by filter paper chromatography is described by Yagi (*190*) In this procedure the flavin derivatives are first determined together by the lumiflavin method and the various derivatives are then separated on paper using 1-butanol with acetic acid as the developing solvent. The fluorometric method was used by Takada (*170*) for determining the riboflavin content in blood.

A critical study of the lumiflavin method for riboflavin has been made by Yagi (*188*). The lumiflavin method has been employed for the estimation of riboflavin in plants (*149*) and in bacteria (*190*). The determination of riboflavin in the presence of other fluorescent substances is accomplished by using appropriate secondary filters (*78*).

The use of cyanogen bromide in place of ferricyanide to convert thiamine to a fluorescent substance *seems to have some* advantages (*55, 171*). The concentration is not as critical and the method is described as rapid and accurate. A 1% solution of harmine is suggested as a new fluorescence standard for the thiamine determination (*77*). The paper chromatography of thiamine has been accomplished at various pH values (*8, 50*) and provides a means of separation from interfering substances. An alkaline methanol solution of ferricyanide is used to develop the chromatogram. An extrapolation procedure for the assay of thiamine in the presence of inhibiting factors such as found in chocolate malt is described by Prokhovnik (*141*). Several new reactions of thiamine which present the possibility of this substance being used as a fluorescence reagent for the analysis of blood and several inorganic ions have been discovered by Wachsmuth (*177*). The possibilities presented are certainly attractive enough to warrant further investigation. The fluorometric determination of nicotinamides is reported to be improved by selective absorption on ion exchange resins (*89, 90*). Paper chromatography has been proved useful in the determination of the metabolic products of nicotinic acid (*86*).

An analysis for urinary pteridine derivatives depends on the fluorescence produced when these substances are oxidized by a milk oxidase (*88*). This is a paper chromatographic method, as is also one described for the xanthopterins by Weber and Hojman (*179*). An improvement on the fluorometric determination of 4-pyridoic acid, in which the sample is treated with alkali after the usual acid treatment in order to obtain a low blank, is reported by Moller (*118*).

Acetoacetic acid in urine can be efficiently determined by the formation of a hydroxycoumarin through the addition of resorcinol in the presence of concentrated hydrochloric acid which is neutralized with sodium carbonate, so that the fluorescence is measured in an alkaline medium (*109*). A modification of the Schlesinger test for urobilin in urine consists of extracting the zinc urobilin complex with chloroform (*99*).

The paper chromatographic and fluorometric determination of gitoxigenin, gitoxin, and purpurea glucoside B is described by Jensen (*85*). The effect of pH and the presence of salts on the fluorescence of terramycin have been shown to be important factors in the determination of this antibiotic in biological media (*157*).

The conjugation of fluorescein with plasma proteins has been shown to be an efficient, practical method of labeling proteins for the microscopic fluorescent observation of their passage in membranes (*151*). The fluorometric determination of the coumarin content of sweet clover has been shown to be very reliable for small concentrations but becomes less accurate for higher levels (*184*).

ORGANIC

A theory of fluorescence as related to chemical constitution of organic compounds has been elucidated by Oda and Yoshida (*130*) in an article in English from Kyoto University. Examples are given in an attempt to show that the intensity of fluorescence is governed by electron mobility and electron density. The quantum efficiencies of organic molecules in solid solution has been determined by Gilmore and his associates (*61*). The fluorescent measurements were made at 77° K. The fluorescent spectra of several polycyclic hydrocarbons at the temperature of liquid air have been recorded by Shpolskiĭ and others (*160*). While it is realized that the above references do not represent analytical methods, it is work of this kind that suggests applications to the analyst.

The research on the identification of the *o*-hydroxycarbonyl compounds which has been in progress in India for some years is being continued. Results are reported (*145*) for the fluorescence of several more types of compounds which combine with boron in concentrated sulfuric acid and produce a fluorescence. Fluorescence tests for carboxylic acids may be conducted by condensation with resorcinol in the presence of a few drops of concentrated sulfuric acid. On diluting with water and neutralizing, a green-orange fluorescence results (*120*). The microchemical detection of 8-quinolinol and its derivatives by contact with aluminum oxide or magnesium oxide has been suggested by Feigl (*41*). A yellowish green to bluish white fluorescence results from either chemical combination or absorption.

A new fluorometric method for the determination of 2-naphthol has been devised by Huter (*80*). A solution of 2-naphthol in concentrated sulfuric acid fluoresces yellow. After standing or heating a blue-violet fluorescence appears which is due to a sulfonated product.

A paper chromatogram of a reducing sugar may be developed by spraying with a 0.3% solution of *p*-aminohippuric acid and heating to 140° C. Common hexoses and pentoses give an orange color which fluoresces strongly under ultraviolet light. Less than a microgram of these sugars can be detected with this reagent or with phthalic acid (*150*).

Benzoic acid can be detected on a paper chromatogram by spraying with salicylic acid and observing the intense blue fluorescence under ultraviolet light (*132*). A fluorescent reaction of acid amides and proteins which may have some analytical applications has been reported by Fujimori (*52*). These compounds with biacetyl produce a characteristic fluorescence.

A fluorescent test for cocaine is evident when cocaine or tropacocaine is warmed with formaldehyde-sulfuric acid; a striking orange-yellow fluorescence results (*129*).

The fluorescence of caffeine and trigonelline is used to observe the separation of these compounds on paper chromatograms before their determination by absorbancy (*100*). Fluorescence measurements have long been used in the determination of quinine. Kostyakov (*102*) and Pechenkin (*134*) have shown the effect of pH and the quenching effect of chloride ion on the fluorescence of quinine. The qualitative and quantitative determination of atabrin and rivanol has also been given further study (*103*).

A fluorometric determination of hydrastine which is based on its oxidation product is reported by Brochmann-Hanssen and Evers to be specific, sensitive, and accurate (*18*). The second in a series of articles by Goodwin and Kavanagh (*64*) on the fluorescence of coumarin derivatives as a function of pH gives data on 54 additional compounds.

The fluorescence of organic compounds as related to functional group analysis is discussed by Heros (*75*). This author concludes that fluorescence spectra in conjunction with changes in fluorescence at various pH values serves as a valuable means of identifying organic groups.

A fluorescence resulting from the photochemical reaction between resorcinol and 2 chloro-4-dimethyl-6-methylpyrimidine can be used to identify the latter. The pyrimidine dissolved in chloroform is spotted on a paper which has been freshly treated with resorcinol solution and is exposed to the radiation of a short-wave mercury vapor lamp. A sky-blue fluorescence results (*49*).

In a review entitled "Development and Prospects of Organic Spot Test Analysis" Feigl (*42*) discusses among other things the possibilities of fluorescence tests for organic compounds.

The fluorescence spectra of 5-aminoacridine hydrochloride shows a continuous emission between 4270 and 5780 A. with a maximum at 4470 to 4650 A. This fluorescence has been applied in the quantitative determination of the compound (*33*).

An investigation into the use of fluorescence in the analysis of petroleum and bitumen has been conducted by Efendiev (*38*). The fluorescent indicator adsorption method for the analysis of petroleum products has been advanced by the work of Criddle and LeTourneau (*26*). New fluorescent dyes have been applied which make the absorption boundary layers on silica gel more defined and the applicability of the method is considerably increased. This same technique has been used in the analysis of lacquer thinners (*26, 39*).

Paper chromatographic methods coupled with observation under ultraviolet light have been found useful in identifying the source of oil slick on river waters (*74, 152*). Katz and Sidorov (*91*) have used the fluorescence of the adsorbed products on an aluminum oxide column for the qualitative analysis of crude oil.

An extensive study of the purification and identification of flavonid pigments has been carried on by Wender and his associates (*22, 34, 57, 186*). Paper chromatography and adsorption on an aluminum oxide column in the quantitative determination of quercetin and rutin have also been used by others (*123, 175*).

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Electroanalysis

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THIS review is a continuation of the previous survey (*5*) and covers the work of 1952 and most of 1953, as well as a few earlier papers which were not covered in the previous review. Although this review covers only a 2-year period, the number of references cited is nearly equal to the number cited in the previous review which covered a 3-year period. A large part of this increased publication rate can be attributed to a rapidly widening interest in the new field of coulometric analysis, but the older and already well-developed methods continue to be extended and improved.

BOOKS AND REVIEW ARTICLES

A comprehensive monograph on electroanalytical chemistry by Lingane (*81*) was published in October 1953. This excellent and timely book covers the theory of electroanalysis, controlled potential electrolysis, internal electrolysis, electrographic analysis, coulometric analysis, potentiometric titrations, and conductometric titrations. The book is devoted principally to a discussion of principles, methodology, and apparatus, although detailed procedures for carrying out several specific determinations are also included. A shorter and less comprehensive review by Lingane (*82*) appeared earlier. West (*147*) has reviewed the applications of electroanalysis in metallurgical analysis. Tutundzhic (*142*) has also reviewed the field, but his paper does not include the latest developments. Reviews of specialized fields of electroanalysis are mentioned under the specific topics to which they pertain.

THEORY

It has not been possible to include in this review a consideration of the papers in the field of fundamental electrochemistry, even though many studies in this field have potential application to electroanalysis. Only those papers dealing specifically with electroanalysis or with the deposition of trace quantities are discussed. Gauguin, Charlot, and Coursier (*60*) have discussed the utilization of polarization curves in electroanalysis.

The study of the deposition of trace quantities of metals from very dilute solutions continues to receive the attention of several groups of investigators. Work in this field has been reviewed by Haissinsky (*69, 70*). Rogers and coworkers (*25, 66, 67*) have reported further results of their studies on the deposition of trace quantities of silver. Curves of cathode potential *vs.* percentage of silver deposited showed plateaus in the region where approximately one monolayer had been deposited (*67*). These workers explain their results by postulating the existence of "active centers" on the electrode surface (*25, 67*). Rogers (*118*) has also studied the distribution of trace elements between an aqueous solution and a mercury cathode in order to shed some light on the mechanism of the deposition process.

Danon and Haissinsky (*38, 39*) and also Coche (*32, 34*) have studied the deposition of trace quantities of bismuth. Both again postulate "active centers" and point out the importance of adsorption in the deposition process. Coche (*32*) has also studied the deposition of lead and polonium. Mills and Willis (*92*) have studied the deposition of traces of several metals by the method of charging curves; this method is extremely sensitive and should prove very useful in further studies in this field.

Lietzke and Griess (*80*) have studied the deposition of ruthenium from very dilute solutions and have postulated a catalytic hydrogen reduction mechanism to explain their results. Schweitzer and Wilhelm (*124*) have studied the spontaneous deposition of radiosilver on various metals. All workers in the field of trace deposition have pointed out that the nature of the electrode surface has a profound influence on the deposition process. Work in the field is greatly hampered by the difficulty of obtaining well-defined and reproducible surfaces.

ELECTROSEPARATIONS

Controlled Potential Separations. The principles and methods of controlled potential electrolysis have been reviewed recently by Ishibashi and Fujinaga (*73*). Most of the effort of the past 2 years appears to have been directed toward the development of improved potentiostats rather than new analytical methods. Bode and his coworkers (*19*) have described the controlled potential electroanalyzer which has recently been made commercially available by the Fisher Scientific Co., Pittsburgh, Pa.

Foster (*52*) has described a simple potentiostat which is very similar to that previously described by Lingane and Jones (*83*), except that the electronic relays employed by Lingane and Jones have been replaced by a single polarized relay. Greenough, Williams, and Taylor (*63*) have designed an elegant all-electronic potentiostat, a modified version of which is now available commercially from Sanford Development Laboratories, Silver Spring, Md.

Kaufman and coworkers (*75*) have also described an all-electronic potentiostat, but the excessive number of tubes required and the high power consumption make the instrument unattractive. Kovalenko (*76*) has described an instrument which not only controls the potential for an ordinary electrolytic separation but also automatically transfers the solution remaining after the separation to a polarographic cell for determination of the minor constituents.

Milner and Whittem (*93*) have given details for the construction of a potentiostat employing components readily available in England. The instrument previously described by Diehl (*44*) has been redesigned by Palmer and Vogel (*112*) to employ English components. Wehner and Hindman (*146*) employed a Brown Electronik amplifier for amplification of the unbalance signal and a motor-driven rheostat for potential control. Coche (*33*) has described a potentiostat with a maximum current capacity of 1.5 ma. for studying electrodeposition from very dilute solutions.

Diehl and Butler (*45*) have devised a method for separating silver from copper by electrodeposition from ammoniacal solution at −0.24 volt *vs.* SCE. Foster (*53*) states that the deposition of zinc at constant potential is more reliable than by the usual constant current methods; the deposition was carried out from ammonium hydroxide–ammonium chloride solution at −1.4 volts for 40 minutes and −1.50 volts for 20 minutes. Lingane and Jones (*84*) separated and determined copper, bismuth, lead, and tin by controlled potential deposition from tartrate medium. Foster (*54*) recommends an electrolysis cell with an isolated anode for the controlled potential deposition of copper from hydrochloric acid solution.

Mercury Cathode Separations. Aylward and Wooldridge (*11*) have described a mercury cathode cell which permits very easy separation of the mercury from the aqueous solution at the conclusion of the electrolysis. Center, Overbeck, and Chase (*30*) employed a magnetic field to achieve rapid countercurrent stirring at the solution-mercury interface. Bock and Hackstein (*18*), Bozon and Bozon (*21*), and Zarinskii (*149*) have also described mercury cathode cells.

The most outstanding recent contribution in the field of mercury cathode separations is that of Bock and Hackstein (*18*), who have made a comprehensive study of the deposition of some 20 different metals. They have detailed the conditions under which quantitative deposition of each is possible and have reported the effect of a number of variables on the deposition process. Alves and Barros (*2*) employed mercury cathode separation of interfering materials prior to the determination of aluminum and of aluminum oxide in steel.

McDuffie and Hazelgrove (*86*) have related the conditions which permit quantitative deposition of manganese. Tsyb (*139*) reported that zinc can be separated from cobalt by depositing both in the mercury cathode and then extracting the zinc by shaking the amalgam with dilute acid. By employing a mercury-plated silver foil rather than a liquid mercury cathode, Hahn (*68*) was able to effect quantitative separation of 10-mg. quantities of copper and iron from 1-mg. quantities of aluminum, uranium, and zirconium in solutions having a total volume of 3 to 5 ml.

Rogers and Merritt (*119*) have studied the deposition of cadmium and thallium into mercury at controlled potentials and have reported the relationship between the cathode potential and the completeness of deposition. Kozlovskiĭ and Tsyb (*77*) studied the potential of a mercury cathode during deposition of copper and bismuth and during subsequent anodic stripping of the deposited metals from the amalgams. The observed potentials were related to the rate of stirring and to the composition of the electrolyte.

Internal Electrolysis. Carpenter and Hopkins (*26*) have given directions for the determination of copper in steel by deposition from sulfuric acid–hydrazine sulfate solution using an iron wire anode. Suzuki (*128*) determined copper in tin-base alloys by deposition from nitrous acid–hydrofluoric acid solution using a liquid lead amalgam anode. Suzuki (*129, 130*) has recommended dilute perchloric acid as the electrolyte for the determination of copper by internal electrolysis with a lead amalgam electrode. This electrolyte was also suitable for the separation of silver and mercury from copper by employing a copper anode. He has given procedures for determining copper and silver in a variety of silver-copper alloys, Duralumin, and copper-base alloys.

Muraki, Kitaoka, and Suzuki (*96*) were able to determine both copper and cadmium in the "zinc" of a dry cell by internal electrolysis employing a zinc amalgam anode. Copper was first deposited from sulfuric acid solution and then cadmium was deposited from an acetic acid–acetate buffer. A method has been devised by Muraki (*95*) for the determination of lead in manganese dioxide. Ishimaru and Mizoguchi (*74*) have pointed out that a solution type anode may replace the usual metal or metal amalgam anode in internal electroanalysis. A platinum wire dipping into a vanadium(II)–vanadium(III) solution served satisfactorily as the anode for the deposition of silver, copper, and bismuth. Schleicher (*121*) has described an apparatus for the performance of internal electrolysis.

Constant Current Electroseparations and Electrogravimetry. The so-called "constant current" methods, together with a few miscellaneous methods, are considered in this section. A very simple electrodeposition apparatus, designed particularly for use in student laboratories, has been described by Elving, Hayes, and Mellon (*48*). Farrington and Pecsok (*51*) have given directions for converting a Heath-Kit battery eliminator into an inexpensive, dual-position, portable electrolysis instrument. Van de Stolpe and van Tongerin (*127*) have described an instrument of conventional design.

In determining traces of antimony in zirconium oxide by a radioactivation method, Hudgens and Cali (*72*) employed electrodeposition from sodium sulfide solution for the final separation of the antimony. Norwitz (*97*) has described a method for the electrolytic separation and determination of bismuth.

Goldberg (*62*) has recommended the use of beryllium nitrate to complex the excess fluoride ion when tin-containing samples are dissolved in nitric acid–hydrofluoric acid. He states that both copper and lead can be determined accurately in fluoride solutions if beryllium nitrate is added. Norwitz has described two methods for the determination of copper, lead, and bismuth in aluminum alloys (*102, 104*), and a method for determining copper and lead in manganese bronze (*101*).

Notvest (*108*) has patented an electrolysis cell designed particularly for the determination of copper and lead. Petrov (*114*) separated small amounts of copper from nickel metal and nickel oxide samples by electrodeposition. The deposited copper was then dissolved in a solution of a ferric salt and the ferrous ion thus formed was titrated with permanganate.

Bastian, Weberling, and Palila (*14*) determined cadmium in zinc-cadmium sulfide phosphors by electrodeposition. In carrying out tracer experiments with radioactive iron, Peterson (*113*) found that the iron could be separated in a form suitable for counting by electrodeposition from oxalate medium. Norwitz (*99*) determined gold by deposition from sodium hydroxide solution. A prior separation of heavy metals was usually necessary.

Suzuki (*131*) has described a method for the determination of traces of iron in soda ash. A solution containing 30 to 40 grams of sample together with tungstic oxide, copper sulfate, and glucose was electrolyzed between platinum electrodes. The iron deposited on the cathode as a copper-tungsten-iron alloy which was then dissolved and the iron determined titrimetrically.

Norwitz (*106*) has shown that lead dioxide deposited at the anode is not appreciably contaminated with manganese provided a high current density at the anode is employed. Interferences from chloride, bromide, arsenic, antimony, tin, and many organic materials in the deposition of lead as the dioxide can be prevented, according to Norwitz and Norwitz (*107*), by fuming with perchloric acid. To remove arsenic, antimony, and tin, hydrobromic acid must also be added, and to destroy organic materials nitric acid together with perchloric acid is recommended.

A technique for the preparation of uniform, adherent deposits of plutonium as the hydrous dioxide on counting plates by an electrodeposition method has been reported by Miller and Brouns (*91*). The plutonium was first oxidized to the plutonyl state in acid solution by ozone and the plutonium then deposited on the cathode from potassium hydroxide solution. Griess (*65*) has found that ruthenium can be quantitatively plated from dilute solutions (not less than $5 \times 10^{-5}M$) of ruthenium nitroso salts. Although this study was not made for the purpose of developing an analytical method for ruthenium, the procedure should be analytically useful.

Broadbank and Winram (*22*) have devised a method for separating and determining silver, copper, and cadmium in silver solder. All depositions were made from perchloric acid solution, the silver at 1.2 volts, the copper at 2.2 volts, and the cadmium at 3.4 volts. No control of cathode potential was employed; the applied potential was merely adjusted with the aid of a voltmeter to the desired values. Norwitz has described one method (*103*) for the analysis of silver solders in which the silver is separated from copper by deposition from a sodium nitrate–nitric acid solution, and another (*98*) in which the silver is separated by precipitation of the chloride which is then dissolved and the silver electrodeposited from cyanide solution.

Anderson (*3*) has reviewed the analytical chemistry of thallium for the period 1940–1950. Electrodeposition and coulometric methods, as well as others, are included. Norwitz (*100*) has described a method for the separation and determination of thallium by deposition as the oxide on the anode from an ammoniacal solution containing copper, which prevents deposition of thallium on the cathode.

Gelfayan (*61*) has devised a qualitative test for tungsten in which the sample solution in sulfuric acid solution is placed in a tube closed at the bottom end with a collodion membrane. When this tube is placed in a beaker of sulfuric acid and an electric current is passed between a platinum cathode in the test solution and a platinum anode in the beaker, the catholyte turns blue if tungsten is present. Theurer and Sweet (*136*) have described an isotope dilution method for the determination of small amounts of zinc in aluminum alloys. The final separation of the zinc for weighing and counting is accomplished by electrodeposition.

Most constant-current separations which have been devised to date depend upon a control of the cathode potential either by suitable adjustment of pH (the cathode cannot become more negative than the potential required for the reduction of hydrogen ion or water) or by addition of nitric acid (which limits the cathode potential to that required for the reduction of nitric acid). Norwitz (*105*) has pointed out that other redox buffer systems could be used for control of the cathode potential. He has found that silver (deposition potential about −0.8 volt) can be quantitatively separated from copper and other base metals by deposition from a solution of a ferric-ferrous redox buffer (redox potential about −0.7 volt). This approach to electroseparations deserves further study and development.

An extension of the electroseparation method to the ultramicro scale has been reported by Alimarin and Petrikova (*1*). These authors have described apparatus and techniques which permit the separation of quantities of material as small as 0.05γ from volumes of solution of the order of 1 μl. They employed both platinum and mercury cathodes in their work.

ELECTRO-OXIDATION AND REDUCTION

Electrodissolution. Beeghly (*15*), in his review on the determination of nonmetallic constituents in metals, has discussed procedures for the anodic dissolution of the sample under conditions such that inclusions of metallic oxides, carbides, and sulfides may be recovered in their original form for further study and analysis. Bertetti (*17*) has described apparatus and procedures for the decomposition of insoluble metallic sulfides by reduction at a mercury cathode. The sulfur in the sample was determined by absorption and titration of the hydrogen sulfide evolved in the decomposition process. Stefanovic and Stefanovic (*125*) have revived the old Gasparini method for decomposing organic compounds by electrolysis between platinum electrodes in nitric acid solution. The authors found this method generally more satisfactory than the classical Carius method for the determination of sulfur in organic compounds.

Preliminary Oxidation and Reduction. Methods employing electrolytic processes in place of chemical reagents to effect preliminary oxidation or reduction continue to receive very little attention. Tomicek and Spurny (*138*) have described a method for the determination of niobium in the presence of tantalum in which the niobium is quantitatively reduced to the tripositive state at a mercury cathode in sulfuric acid solution. The reduced solution was treated with ferric iron and the resulting ferrous ion titrated with ceric sulfate.

Electrographic Analysis. An excellent and comprehensive review of the theory, apparatus, and methods of electrography and electro-spot testing has recently been published by Hermance and Wadlow (*71*). A brief historical review by Monk (*94*) has also appeared. Kronstein (*78*) has described electrographic methods for testing organic protective coatings on steel. Clark and Hale (*31*) have devised an electrographic scheme of qualitative analysis for the identification of alloys and stainless steels. Stemprok (*126*) has applied a capillary method to the electrographic analysis of ores.

COULOMETRIC TITRATIONS

The relatively new field of coulometric titrations and analysis has undergone a spectacular growth during the past 3 years and has attracted the attention of many new investigators. Progress in the field has been reviewed by Cruse (*37*), Greuter (*64*), and Tutundzhic (*140*). A theoretical analysis of coulometric titration processes has been given by Delahay (*43*). The utilization of polarization curves in deducing the proper conditions for carrying out coulometric titrations has been discussed by Badoz-Lambling (*12*) and by Gauguin and Charlot (*59*). Tutundzhic (*141*) has proposed that chemical primary standards be replaced by the coulomb for all titrimetric analyses.

Primary Processes. A primary coulometric titration is one in which the substance to be determined reacts directly at the electrode. The analysis depends upon a measurement of the number of coulombs required for a quantitative electrolytic reaction. Usually it is necessary to control the potential of the working electrode in analyses of this type, although in some cases constant current techniques may be used. MacNevin (*89*) reviewed the field of primary coulometric analysis in a recent symposium.

MacNevin and Baker (*87*) have reported successful determinations of iron(II) and arsenic(III) by primary coulometric titration with controlled anode potential. These investigators found that it was not necessary to carry the titration to completion, since the total number of coulombs required for the titration could be estimated graphically with good precision from a log current-time plot of data taken during the first 10 to 15 minutes of the titration. MacNevin, Baker, and McIver (*88*) determined both chloride and bromide simultaneously in mixtures by coulometric titration at a silver anode followed by weighing of the deposited silver halide mixture. Kumze and Willey (*79*) have described a coulometric method involving anodic stripping for the determination of tin and tin-iron alloy weights in tin plate.

Tödt (*137*) reported a coulometric technique which he claimed was sufficiently sensitive to detect one thousandth of a monomolecular layer of oxygen or oxide on a metal surface. The metal surface served as the cathode and an isolated cadmium rod was employed as the anode. No external source of electrical power was required. The electrolysis current was measured by a sensitive light-beam galvanometer and was automatically recorded on a revolving drum.

Lord, O'Neill, and Rogers (*85*) determined submicrogram quantities of silver in volumes of 20 μl. to 25 ml. by electrodeposition onto a platinum cathode for a measured period of time followed by anodic dissolution of the deposit. From recorded current-time curves the number of coulombs required for the dissolution process could be measured. The quantity or the concentration of silver in the sample solution was then determined from calibration curves. A similar technique was employed by Gardiner and Rogers (*58*) for the determination of submicrogram quantities of cadmium and zinc. For the latter determinations the smooth platinum electrode employed in the silver work was replaced by a mercury-plated platinum electrode.

Schwabe and Seidel (*123*) have described a coulometric method for the determination of the γ-isomer of benzene hexachloride. The method involves electrolysis of the sample under carefully controlled conditions in a special cell and measurement of the time required for the electrolysis current to decrease to a predetermined arbitrary value. The measured time is proportional to the amount of γ-isomer in the sample.

Secondary Processes. A secondary coulometric titration is one in which there is generated at one of the electrodes of an electrolysis cell a suitable chemical intermediate which is then allowed to react with the substance to be determined. Processes of this type are usually carried out at constant current, and the time required for the titration is measured. The number of coulombs is then calculated from the current-time product. The chemical intermediates may be generated either internally at an electrode dipping into the sample solution or externally in a suitable electrolysis cell from which the intermediate is delivered to the sample solution.

Several new coulometric intermediates have been reported. Arthur and Donahue (*4*) have found that titanous ion can be generated with 100% current efficiency from titanic chloride solutions at a gold cathode. They employed this reagent for the reductimetric titration of ferric iron. Farrington (*49*) has reported that copper metal is a satisfactory intermediate for the determination of iodine. His technique involves plating a known amount of copper onto a platinum electrode from a cuprous iodide solution. The iodine sample, or a sample of any oxidizing agent which will react with the cuprous iodide solution to form iodine, is then added and allowed to react with the copper metal. The excess copper is then coulometrically stripped from the platinum electrode and the amount of copper reacting with the sample is calculated from the difference between plating and stripping times.

DeFord and Horn (*41*) have generated manganic ion from manganous sulfate–sulfuric acid–phosphoric acid solution and have employed this strong oxidizing intermediate for the titration of iron, arsenic, and oxalate. Pitts and coworkers (*115*) have designed a new cell for external generation and have employed this cell for the generation of iodine, bromine, and chlorine at currents of several hundred milliamperes.

A large number of new titration methods employing previously reported intermediates have been described. Badoz-Lambling (*13*) has reported a coulometric method for determining the titer of hydrochloric acid solutions.

Oelson and Graue (*109*) have described an internal generation method for the determination of small quantities of acids and bases. They employed a platinum electrode dipping into the sample solution and a carbon electrode isolated from the sample solution by a collodion membrane. The carbon electrode compartment was flushed continuously with a neutral electrolyte in order to prevent acids or bases which were generated at this electrode from diffusing into the sample. Sulfur and carbon in steels and in organic compounds were determined by titrating the sulfuric and carbonic acids formed by absorption of the combustion products. Quantities of sulfur and carbon in the range 0.02 to 2.5 mg. could be determined. For the determination of small amounts of acids and bases this internal generation technique appears to be superior to the external generation technique previously described by DeFord and coworkers (*42*). In an earlier paper Oelson and coworkers (*110*) described a similar but somewhat simpler procedure for titrating carbonic acid, and in a later paper (*111*) reported a titration cell which made use of a zinc anode and required no external source of current. The titration current was regulated by adjusting the depth of immersion of the anode. The latter cell was also employed for the determination of oxidizing agents. Schleicher (*122*) independently reported a similar zinc anode cell which he used for the titration of permanganate with ferrous iron as the intermediate.

Procedures for the coulometric titration of thiosulfate with iodine have been described by Rowley and Swift (*120*) and by Tutundzhic and Mladenovic (*143*). Carson (*28*) has employed bromine as the intermediate for automatic titrations of 0.01- to 7-mg. quantities of uranium.

Buck, Farrington, and Swift (*23*) reported that thallium can be titrated successfully with either bromine or chlorine. Buck and Swift (*24*) have developed a method employing dual intermediates for the bromometric determination of aniline and similar compounds which react slowly with bromine. Bromine was first generated anodically in slight excess, and after allowing time for complete reaction with the sample, the excess bromine was titrated with cathodically generated cuprous copper. The equilibria involved in the cupric bromide solutions employed for the generation of these dual intermediates have been discussed by Farrington, Meier, and Swift (*50*).

Furman and coworkers have employed electrolytically generated ceric ion for the titration of microgram quantities of uranium (*56*), and of hydroquinone and *p*-methyl aminophenol sulfate (Metol) (*55*). The use of ferrous iron for the titration of vanadium in uranium (*57*) and for the titration of permanganate (*36*) has been described by Furman and coworkers. Meites (*90*) has employed ferrous iron for the titration of ceric, dichromate, permanganate, and vanadate ions.

Apparatus. An improved constant-current power supply for coulometric titrations has been designed by Reilley, Adams, and Furman (*116*). Cooke, Reilley, and Furman have described a sensitive method for locating the equivalence point in coulometric titrations (*35*). An elegant automatic titrator, designed particularly for the coulometric determination of small quantities of uranium, has been described by Carson (*27*). An automatic titrator employing amperometric detection of the equivalence point has been constructed by Richter and Swift (*117*).

Wise, Gilles, and Reynolds (*148*) employed photometric detection of the equivalence point in their automatic titrator. Carson (*29*) has described a universally applicable device for end point anticipation in automatic titrations. An instrument for coulometric titrations has been patented by Eckfeldt (*46*). The general field of instrumentation for coulometric titrations has been discussed by DeFord (*40*).

Meites and coworkers (*20, 90*) have employed a Weston integrating relay as a coulometer. A gas microcoulometer has been described by Berkes (*16*). Syrokomskiĭ and Nazareva (*132*) recommended a vanadium coulometer which is stated to compare favorably with a silver coulometer and to be easier to use. Taft and Liese (*133–135*) have designed an iodine coulometer and have made a very careful study of its relability. Ehlers and Sease (*47*) have described a coulometer in which the current to be integrated is employed to plate copper onto a platinum cathode. The deposited copper is then stripped automatically at constant current and the number of coulombs calculated from the current-time product for the stripping process.

Continuous Automatic Titrations. Although the coulometric method offers very attractive possibilities for continuous automatic titrations in flow processes, very little work in this field has been reported to date. Austin and coworkers (*6–10, 144, 145*) have presented a detailed description of the Titrilog, a continuous automatic recording titrator employing electrolytically generated bromine as the chemical intermediate. This instrument has been employed for monitoring the concentrations of a variety of sulfur compounds in gas streams.

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Inorganic Gravimetric Analysis

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RESEARCHES on 56 elements in the past two and a half years have yielded advances in the discovery of new precipitants and in the development of interfering reagents. While there has been no record of new types of precipitating reagents nor of many reagents of high specificity, considerable interest has been indicated in the analytical function of derivative groups in organic precipitants. Thermodynamic measurements are eliminating the trial and error search for improved selectivity and specificity.

For those engaged in the routine practice of analytical chemistry the reconnaissance surveys will be enlightening. The more numerous investigations of this nature now appearing will give better delineation to the precision and accuracy of accepted procedures and provide an improved perspective for analytical chemists.

GENERAL PROCEDURES

Preparation of Samples and Precipitates. The chlorination of samples as a method of corrosion is finding wide application, particularly for those materials which resist the usual methods of attack or where corrosion involves the introduction of undesirable impurities. Atkinson, Steigman, and Hiskey (*10*) used chlorination to establish the groundwork for a new system of analysis of niobite minerals. In the absence of iron, the method involved chlorination by octachloropropane at 300° C. and separation by distillation of tin and titanium from mixtures of niobium, tantalum, and related elements.

In a later study (*126*), two methods of eliminating the catalytic interference of iron were proposed. In one, iron and manganese were removed as sulfides from ammoniacal tartrates. In the second, somewhat more satisfactory approach, the iron and manganese were retained in solution by complexing reagents. The authors found that in a specific series of the periodic table—e.g., titanium, vanadium, and chromium, each in its highest valency—the ease of chlorination increased with the atomic number. In any one column the ease of chlorination decreased with increasing atomic weight.

Hiskey and associates (*127*) observed that with very basic oxides such as barium oxide the chlorination failed completely, although in mixtures of oxides the more acidic oxide assisted the chlorination of those less easily chlorinated. The presence of tantala in the niobia-titania mixture hindered chlorination of titania, and strangely the presence of zirconia in certain proportions practically prevented over-all chlorination; on the other hand, stannic oxide had a beneficial effect. As might be expected, amorphous oxides chlorinated more readily than oxides which had been ignited at high temperatures. The authors concluded that the reactivity of the oxides was enormously improved by a low temperature hydration.

Another approach to the problem of corroding niobium and tantalum minerals was discussed by Treadwell *et al.* (*307*). These authors used dry chlorination by heating at 500° C. for 8 hours in a current of hydrogen chloride gas charged with carbon tetrachloride. Titanium(IV) chloride was thus isolated, and following reduction of iron, the hydroxides of niobium and tantalum were precipitated.

To corrode earth acid oxides Schäfer (*263–265*) and coworkers used carbon tetrachloride in a sealed tube at 280° C. to produce the pentachlorides of niobium and tantalum and the tetrachlorides of tin and titanium. The latter two salts were selectively sublimed under vacuum at 100° C. The pentachlorides were then sublimed, weighed, converted to the oxides, and weighed again, and from the two equations the weights of the two metals were calculated. Other methods of separation were also discussed. All of these investigations merit the attention of analytical chemists interested in the dissolution of the many unreactive oxides and metals.

An interesting application of chlorine was made by Preis (*219*) who used the dry, oxygen-free gas to distinguish silica from the silicon present as calcium silicide. The latter was converted to silicon tetrachloride at 115° to 130° C.

For the sodium peroxide fusion of ores, zirconium crucibles were recommended by Petretic (*212*). The corrosion of the crucible per gram of sodium peroxide amounted to about 5 mg. of zirconium as compared to 250 mg. for crucibles of nickel, iron, or silver. Zirconium crucibles machined from de Boer process zirconium bar were more corrosion-resistant and expensive than those prepared from U. S. Bureau of Mines vacuum-cast metal. For the corrosion of silicates, alkaline earth sulfates, and lead sulfate, Mehlhose (*186*) used metallic sodium.

Gordon (*104*) reviewed the advantages of homogeneous precipitation. Because of the control of changes of acidity, one could sometimes utilize a two-stage precipitation which was comparable in effect to double precipitation.

Villanova (*327*) reviewed literature dealing with filtration in analytical chemistry. Suitable ignition temperatures for the oxalates of magnesium, zinc, cadmium, manganese, cobalt, and nickel were determined by Kawagaki (*143*).

Bigg and Burch (*29*) have provided some very useful information concerning the stability of various types of analytical weights. Weights of a specially highly polished stainless steel were superior to austenitic stainless steel or nonmagnetic nickel-chromium. Chromium plated weights, while retaining a better appearance, possessed a magnetic undercoat. Lead should not be used to adjust weights. Plain polished or lacquered brass weights were unsatisfactory as laboratory standards.

Armstrong (*8*) discussed methods of eliminating errors in weighing which were due to electric charges developed on heating silica crucibles. Methods of avoiding the electrostatic charges on glass and other vessels were also discussed by Hadfield and Bigg (*115*).

General Gravimetric Reagents and Selective Methods of Separation. The use of nicotine thiocyanate reagent in inorganic analysis was discussed by Burkat, Skrynnik, and Yaroslauskaya (*42*). They described the physical and chemical characteristics of precipitates formed by copper, cadmium, cobalt, nickel, zinc, manganese(II), and iron. In general the precipitates were initially amorphous, becoming crystalline, but reverting to an amorphous condition upon treatment with caustic solutions.

Pallaud (*206*) discussed the properties and uses of dioximes and monoximes of the α-diketones. Kuraš and Ruzicka (*160*) described the precipitating reactions of α-phenylacetamidoxime with copper(II), mercury(II), iron(II), and osmium(VIII). The use of salicylalamines for the precipitation of lead, vanadium(II), uranyl ion, and lanthanum was recorded by Terent'ev and Rukhadze (*304*). Modified procedures for the precipitation of copper and nickel by salicylalamines were included; and in a second study (*303*) the authors recorded the variations in solubilities, etc., of the copper and nickel salts of a homologous series of salicylalkylamines.

The use of disalicylalpropylenediamine for the precipitation of copper and nickel was recorded by Terent'ev, Rukhadze, and Fadeeva (*305*). The large formula weights of the precipitates suggest that the method may be useful for small amounts of the metal. Other aliphatic and aromatic salicylamines were included in the investigation.

Endo and Mashima (*76*) made the interesting observation that the addition of a methyl group to salicylaldoxime or salicylaldehyde resulted in inability to precipitate cadmium or zinc. It was recorded also that precipitation at lower pH values occurred when aldehyde or ketone groups were converted to an oxime.

Malissa (*178*) stated that penicillin precipitated some 16 metal ions including silver, gold, and some of the platinum metal group. Gagliardi and Loidl (*90*) used thioformamide in an acetic acid medium to precipitate copper sulfide in the presence of arsenic(V). The latter was isolated from the filtrate by a strong hydrochloric acid solution of thioformamide. Flaschka (*81*) summarized the use of thioacetamide for the precipitation of sulfides of some 17 cations. This reagent possesses the advantages associated with the relatively slow internal production of the precipitating anion and is worthy of some consideration.

The effect of α-methyl substitution on the 8-quinolinol molecule was discussed by Borrel and Paris (*32*). They also determined the composition of precipitates formed by 2-methyl-8-quinolinol with magnesium, copper, zinc, nickel, cobalt, thallium, vanadium, and molybdenum. Suzuki and Yoshimura (*292*) examined the optimum acidity for the precipitation of benzoates of aluminum, cerium, chromium, iron, tin, titanium, thorium, and zirconium. They also determined the masking effects of tartaric, oxalic, and citric acids. In the presence of tartaric acid, titanium and aluminum could be separated from solutions containing the above cations.

The application of diantipyrylphenylmethane to the determination of hexacyanoferrate(III) was discussed by Gusev and Beĭles (*112*). Precipitation was made in sulfuric acid solution, and the precipitate was dried at temperatures beyond the aqueous dissociation temperature of the hydrates (110° to 120° C.). A procedure for the determination of the tetravalent anion in the presence of the trivalent anion was included.

Freiser (*85*) recorded a useful contribution concerning the analytical application of 2-(*o*-hydroxyphenyl)-benzoxazole and of 2-(*o*-hydroxyphenyl)-benzothiazole; the latter was more selective as a precipitating agent for metal cations, reacting only with copper in acetic acid–acetate buffer and only with cadmium in sodium hydroxide–sodium tartrate buffer. The action of 8-hydroxyquinaldine on the elements of Group III and other ions, was recorded by Phillips, Emery, and Price (*213*). Indium, scandium, thorium, uranyl, and lead ions were quantitatively precipitated. Yttrium, gallium, beryllium, and zirconyl ions were partially precipitated. West (*340*) reviewed the application of 26 new organic precipitants for some 20 cations.

Vanossi (*319*) published a procedure for the analysis of the iodide group, platinum, palladium, tellurium, silver, lead, indium, bismuth, copper, and cadmium. Extractions were made with solvents such as ether and ethyl acetate, and various standard methods of precipitation were applied. Rây (*237*) used an arrangement of conventional methods for the separation of iron, aluminum, and titanium. For the separation of iron and aluminum from certain bivalent elements Šušić and Njegovan (*290*) reduced the expense involved in the $HgNH_2Cl$ method of buffering the solution.

The analytical applications of fluoberyllate ions were discussed by Feigl and Schaffer (*77*). These included simplifications in the analysis of fluorspar and cryolite and the detection of beryllium in minerals, ores, and alloys. Researches of this type which involve the application of specific interferences are increasing in number and are of significant theoretical and practical value.

A second example of this approach to separations is the extensive work of Přibil (*220*) and coworkers who evolved numerous separations by developing metal complexes with ethylenediaminetetraacetic acid and triacetoamine. These separations included the isolation of silver and thallium from lead, bismuth, copper, and iron(III); manganese from nickel, zinc, and cobalt; and the determination of tungsten by 8-quinolinol in the presence of various elements of Groups II, III, VI, VII, and VIII (*226*).

Analytical Methods for Specific Materials. A lime method for the determination of alkali metals in silicates was described by Babko and Romanishina (*13*). The residue from hydrofluoric acid treatment, consisting of fluorides and fluosilicates, was treated with sufficient calcium hydroxide to turn phenolphthalein red and the mixture subsequently filtered. Calcium was removed from the filtrate by carbon dioxide, and the alkali metals were determined in the filtrate either by evaporation and weighing or volumetrically.

The fact that silicides and carbides when fused in an inert atmosphere with sodium hydroxide produce hydrogen stoichiometrically was used by Schwarz, Johann, and Zörner (*269*) for the determination of iron silicide, silicon carbide, and silicon dioxide in the presence of each other. As one alternative the hydrogen was oxidized to water by copper oxide. Control methods for the analysis of complex sulfide ores were discussed by Pinkerton (*215*). These included methods of assay for gold and silver.

Raistrick, Harris, and Lowe (*232*) used gravimetric determinations in new procedures for the analysis of commercial triphosphate. Fongi (*83*) discussed certain time-saving operations used in dissolving cast iron prior to the determination of manganese, phosphorus, and silica. West (*339*) published a review dealing with the recent progress in extraction and precipitation methods in metallurgical analysis.

The present method of calculating the composition of hydrated dolomitic lime was evaluated critically by Clark and Sprague (*51*). They concluded that if adsorbed water was determined from loss in weight at 280° instead of 120° C. as now recommended and other precautions were observed, the results supported the validity of computing the percentages of calcium and magnesium hydroxides from the content of combined water. This research involved the use of a variety of methods and will be of special interest to those concerned with the physical characteristics of plaster.

To avoid oxidation of coal during the determination of moisture, Deinum and Goedkoop (*56*) heated the sample at 105° C. in a stream of oxygen-free nitrogen. Excellent results were obtained by either weighing the anhydrone or by weighing the residual coal sample. Bozon and Bozon (*34*) recorded a procedure for the determination of aluminum in ferrosilicon and silicoaluminum. Iron was removed by a mercury cathode, titanium was precipitated by cupferron, and aluminum by 8-quinolinol.

Theories of Precipitation and New Aids. Freiser (*85*) discussed, among other things, the relationship of chelate stability to the selectivity of an organic precipitating reagent. Evidence was offered to indicate that decreased chelate stability can result in greater selectivity and that a search for specific reagents would be more fruitful among those reagents in which steric hindrance can operate and the apparently less stable six-membered ring arrangement occurs. The suggestion was made that the expression of the solubility equilibria should differentiate between stability and solubility.

Yatsimirskiĭ (*343*) used the energy characteristics of ions to classify precipitating reactions. On the basis of the electrostatic and covalency "indexes" these reactions were divided into four groups. Cations with a small electrostatic index were precipitated by large anions; cations with a small electrostatic index but with a high covalency index were precipitated by univalent ions with a small electron affinity; cations with a high covalency index were precipitated by anions having a tendency to form covalent bonds; cations having both indexes large required reagents which formed intermediate types of bonds.

In a second study Yatsimirskiĭ and Astasheva (*344*) used large anions to precipitate large complex metal cations. The compositions of the precipitates were $M[CS(NH)_2]_nX_n$. M could be silver, thallium, copper, mercury, cadmium, lead, or bismuth, and X could be $Cr(NH_3)_2(CNS)_4$, $Co(NH_3)_2(NO_2)_4$, or picrate. Some of the characteristics of the precipitates were described. It would be of value to know whether or not these precipitates had constant composition.

The difficulties encountered in the calculation of the solubility products by applying thermodynamic data were discussed by Tananaev, Mizetskaya, and Vinogradova (*298*). In systems such as lead sulfate–thorium nitrate–lithium sulfate–water in which complex ions were formed, the solubility could be calculated fairly closely by using the dissociation constants of the complex ions formed. In a great many cases this approach is ineffective because the composition of the dissolved complex is unknown.

Borrel and Paris (*33*) studied the precipitation properties and determined the approximate solubility products of some metallic 8-hydroxyquinolinates and 2-methyl-8-hydroxyquinolinates. Fischer (*79*) examined by electron microscopy the physical characteristics of barium sulfate precipitates. He found that digestion at room temperature produced no marked change in general shape, degree of perfection, or size of particle. Ostwald ripening did not occur because the usual conditions of precipitation produced crystals beyond the limit of 1 micron. The influence of coprecipitated impurities was studied. Various suggestions were made to account for the protuberances which appeared when barium sulfate was precipitated in the presence of sodium chloride, sodium nitrate, and ferric chloride.

The application of radioactive cations to determine the characteristics of coprecipitation phenomena are increasing in number. For the precipitated system barium chromate–strontium sulfate, Miller, Neyman, and Sazonov (*189*) used this technique to determine the relationships among acidity, ratio of barium to strontium, and degree of coprecipitation. Interesting discussions on the "filterability" of precipitates were recorded by Nikolaev and coworkers (*202*). The filtration coefficient k, in centimeters per second, was defined in terms of the various characteristics of the solution and the precipitate and of the time of filtration and determined as a function of the time required for precipitation. From these studies the authors drew conclusions concerning the factors which affect the growth, size, adsorption, and stability of crystals.

In another study Nikolaev (*201*) recorded the filtration indexes of calcium sulfate and the hydroxides of magnesium, iron, and aluminum. These investigations include much interesting material.

Duval (*66*) recorded a review of his publications dealing with continuous weighing in analytical chemistry. While the authors cannot agree entirely with the "tone" of the article nor accept all of the statements recorded, the publication is an important one and should be examined in detail by analytical chemists. Reference to most of the subject matter has been made in previous reviews on inorganic analysis; however, there are included additional data of some significance.

Duval discussed three interesting cases of oxygen adsorption.

The first occurred during the decomposition of ammonium chloroplatinate, and it is stated that at 538° "the metal takes up oxygen, doubtless coating itself with PtO." The initial weight of the metal is regained at 811°. In the second case, it was found that finely divided gold heated in air "from room temperature up to 950° to 980°, takes up oxygen and releases it on cooling." Third, under the heading "A curious oxidation phenomenon" dealing with the effects of progressively heating certain oxidants such as nitrates and chromates, there is observed an initial gain in weight from the oxygen of the air. The author states, "Therefore, when a compound is to give up oxygen, it begins by taking a small quantity of this element from the air to form an unstable peroxide or persalt, which doubtless is capable of starting a chain decomposition."

The increase in weight of finely divided platinum on heating in air is not an unknown phenomenon. In general, this has little analytical significance, but it should be noted that the literature contains no experimental data whatever which could permit the statement that the coating is monovalent platinum oxide.

Schlecht (*266*) recorded the results of a "reconnaissance survey" of the present state of rock analysis. The author states that "this work is indeed the first step in arriving at ranges for the precision and accuracy of a rock analysis, but much work lies ahead before that aim is accomplished." The study could be examined profitably by mineralogists and geologists who estimate the value of an analysis by the departure from a summation of 100%. Twenty-five laboratories of good repute participated in the analysis of a sample of a granite and a sample of a diabase. It was found in some cases that when summations were near 100% there were variations in percentage of alumina and silica, while some of the analyses with extreme summations gave fairly good silica and alumina results. In general, silica determinations were apt to be low while those for alumina were often high. Hartford (*122*), dealing with industrial chrome ore analysis with a view to reducing the discrepancies between laboratories, provided records of comparative analysis of ore shipments kept for 8 years. Such cooperative investigations in various other fields of analysis would yield great profit. The practicing analyst is often too prone to confuse the terms precision and accuracy.

LIGHT ALLOY ELEMENTS

Lithium, Beryllium, and Magnesium. Kato and Hagiwara (*116, 117, 139–141*) investigated the extraction and determination of lithium. Differing from sodium chloride, lithium chloride showed high solubility in *n*-butyl alcohol, butyric acid, methyl acetate, castor oil acetate, olive oil acetate, and diethylamine (*139*). Aluminate reagent (*141*) was used to precipitate lithium in a medium whose pH was 11.0 to 11.5. The product was ignited to $Li_2O.2Al_2O_3$. The possibility of determining lithium as a metal salt of a fatty acid was studied and rejected (*140*). The authors also recorded a procedure (*139*) for determining lithium in lepidolite. After removal of the acid sulfide and alkaline earth groups, lithium was extracted with *n*-butyl alcohol and finally converted to the sulfate.

Grüttner (*109*) found that for small quantities of lithium the zinc uranyl acetate method was superior to the phosphate, sulfate, or lithium (2:5) aluminate methods. The zinc uranyl acetate reagent was also used by Shigematsu, Kimura, and Yasumaru (*271*). Before filtering, the mixture was retained at 100% relative humidity for 24 hours. The solubility in ethyl alcohol wash water required a correction factor. Nickel uranyl acetate reagent was similarly used (*272*). The precipitate was not a pure substance and an empirical factor was required. An advantageous modification required the determination of the nickel in the washed precipitate by a colorimetric method.

Methods for the determination of beryllium were examined by Airoldi (*2*). The pyrophosphate was recommended and certain modifications were introduced. Arising from Přibil's extensive application of ethylenediaminetetraacetic acid, "complexone," as an interfering reagent, a rapid method for the determination of beryllium in beryl has been developed by Huré, Kremer, and Le Berquier (*133*). The obvious advantage of the method is the extensive elimination of associated interferences. The authors preferred precipitation as the phosphate because there was less adsorption of impurities and the presence of phosphate in the mineral did not necessitate a preliminary separation.

Ethylenediaminetetraacetic acid was applied to advantage in the separation of beryllium, titanium, and uranium. In this procedure Přibil and Adam (*221*) isolated these constituents by precipitation by ammonia in the presence of ethylenediaminetetraacetic acid. Subsequently hydrated titanium(IV) oxide was removed, followed by beryllium and then uranium.

Following the precipitation of aluminum and iron by 8-quinolinol, Castello (*46*) removed excess of reagent by addition of copper acetate prior to the precipitation of beryllium hydroxide. For the determination of beryllium in beryl, Brewer (*35*) found the 8-quinolinol method time consuming. The precipitation of the hydroxide in the presence of ethylenediaminetetraacetic acid was accomplished with acceptable accuracy. However, the accuracy obtained was fortuitous in that the ignited oxide contained silica and small quantities of iron, aluminum, platinum, and sodium, which were about equal to the weight of beryllium lost during fusion and precipitation. This same condition applies to the 8-quinolinol procedure. The new procedure, however, yielded greater precision and required less time. With a large excess of reagent an almost complete separation was made in the presence of iron, manganese, chromium, calcium, magnesium, and aluminum. Two milligrams of titanium introduced no interference. With larger amounts the ignited residue was treated to determine titanium colorimetrically.

Akiyama (*3*) improved the precipitation of beryllium hydroxide by adding ammonium nitrite and methyl alcohol and subsequently volatilizing methyl nitrite. This author (*4*) also examined the conditions of precipitating, washing, and igniting beryllium hydroxide obtained by four recommended methods and recorded a procedure for the determination of beryllium by hexamethylenetetramine (*5*). Gallagher (*95*) described a procedure for the analysis of beryllium carbide to determine total beryllium, beryllium oxide, free carbon, combined carbon, nitrogen, and water.

The effects of temperature on precipitation of magnesium hydroxide were discussed by Vinogradova (*329*). Initial precipitation occurred at increasing acidities as the temperature was increased from 0° to 60° C. Rocha Vaz and Nóvoa (*243*) recorded a procedure for the determination of magnesium by 8-quinolinol. To separate magnesium from copper, iron(III), and manganese(II) by precipitation of the 8-quinolinolates, Tanaka and Hayashi (*296*) recommended various optimum ranges of acidity.

Kitahara (*145*) determined small quantities of metallic magnesium in nickel by volatilizing magnesium along with some nickel, separating the latter as a sulfide, and precipitating magnesium as phosphate. Egido (*74*) and Maekawa (*173*) recorded procedures for the determination of magnesium in nodular iron. In both cases standard methods of separation of iron, copper, and other elements were applied. Abbey (*1*) discussed methods for the determination of magnesium in calcium metal. The methods examined were the pyrophosphate, 8-quinolinol, spectrographic, alkalimetric, and colorimetric. It was concluded that for maximum accuracy either the classical gravimetric pyrophosphate method or the volumetric oxalate-quinolinol method was acceptable.

As one of a series of methods for the analysis of aluminum and its alloys, the British Standards Institution recorded a procedure for determination of magnesium (*39*). Depending upon the proportions of silicon present in the metal, two preliminary separations of aluminum were performed. The magnesium residue was purified by a mercury cathode method followed by treatment with ammonium hydroxide and peroxysulfate. Procedures were included for determining calcium and traces of magnesium in the ignited magnesium pyrophosphate.

Aluminum. Ripan and Parvu (*241*) recommended a procedure for determining aluminum and other trivalent elements which involved treatment of the solution with alcoholic benzoic acid and hexamethylenetetramine. The precipitate was dried at 100° to 105° C. and weighed. The ignited aluminum oxide was less hygroscopic than that obtained by classical methods.

The precipitation of aluminum as lithium aluminate was discussed by Oka and Murata (*205*). Precipitation was complete at pH 7.4 to 9.0 and at 7° to 20° C. The ignited precipitate had the composition $Li_2O.2Al_2O_3$. Sodium mercaptobenzothiazole was used by Spacu and Pirtea (*282*) to precipitate aluminum. The precipitate was dried at 105° to 110° C. and weighed. An examination of various conditions affecting the precipitation of aluminum as phosphate was discussed by Saxer and Jones (*262*). An improved procedure applicable to iron ores was described.

A procedure for the determination of aluminum oxide in pure aluminum was recorded by Werner (*337*). Aluminum was selectively extracted by methyl alcohol and bromine. This solution was also used in a procedure for the determination of aluminum oxide in permanent magnetic alloys (*38*). The residue from the extraction was fused with potassium hydrogen sulfate and treated with sulfuric acid; following removal of iron and titanium with cupferron, aluminum was recovered as the 8-quinolinolate.

For the separation of aluminum from moderate amounts of iron, Hummel and Sandell (*132*) improved the accuracy of the precipitation of aluminum hydroxide in the presence of thioglycolic acid (mercaptoacetic acid). Less iron was coprecipitated when ferric iron was reduced by sulfite prior to the addition of thioglycolic acid. Excessive digestion destroyed the latter and resulted in a precipitate of ferrous sulfide. Although the urea-succinate method was better suited for the separation of aluminum from large amounts of iron, the proposed method offered the advantage that titanium and phosphate were completely precipitated, thus permitting the determination of aluminum by difference. Direct determination of iron in the filtrate was not accomplished.

For the determination of aluminum in steel, Aven and Freiser (*11*) isolated most of the iron by extracting the thiocyanate complex with butyl phosphate. To determine aluminum in low iron alloys, Tananaev and Yakovlev (*299*) precipitated aluminum fluoride from a sulfuric acid solution of the mixed hydroxides containing ammonium oxalate and citrate. The fluoride precipitate was dissolved with a solution of boric and hydrochloric acids and the aluminum isolated finally by 8-quinolinol. The procedure was modified for the determination of aluminum in steels and ferrous-base alloys.

Kinnunen and Merikanto (*144*) discussed various control methods for the determination of aluminum in copper-base alloys. One of the three proposed methods involved the gravimetric precipitation of aluminum by 8-quinolinol and subsequent ignition at 1200° C. in the presence of oxalic acid. The influence of silicic acid on the 8-quinolinol method was discussed by Dubrovo (*63*). It was observed that polymerized silica obtained from aged acid solutions could result in positive errors of 100%. This error could be avoided by a pretreatment of the solution with sodium hydroxide to convert silicic acid to the unimolecular state. The homogeneous precipitation of aluminum by 8-quinolinol was accomplished by Stumpf (*287*) who used urea to obtain a filtrate of pH 4.4 to 5.6.

RADIOACTIVE ELEMENTS

Thorium, Niobium, and Plutonium. A large number of reagents for the precipitation of thorium have now been recorded in the literature. A critical evaluation of these would be a useful contribution. Researchers at Andhra University, Waltair, South India, have added to this too lengthy list. Separation of thorium from cerite earths by *o*-toluic acid and acetylsalicylic acid were described by Rao and Rao (*236*); with the latter reagent reprecipitation was required if the cerium to the thorium ratio was greater than 5. Krishnamurty and Rao (*151, 152*) separated thorium from uranium and from cerite earths by anisic acid in neutral solution. If the proportion of uranium to thorium exceeded 2 to 1, double precipitations were required.

Venkateswarlu, Purushottam, and Rao (*326*) found that by double precipitation cinnamic acid separated thorium from 350 times as much uranium. Krishnamurty and Verkateswarlu (*153*) also used cinnamic acid to separate thorium from cerite earths. Other new aliphatic reagents recorded were adipic and succinic acids (*287*), the latter having lesser value for separations from rare earth elements. New aromatic reagents recorded were vanillic acid (*150*); *m*-cresoxyacetic acid (*323*); ammonium picrate and ammonium 2,4-dinitrophenol (*235*); camphoric acid (*197*); ammonium furoate and sodium sulfanilate (*161*); pyrogallic and *m*-hydroxybenzoic acids (*58*).

Murthy, Rao, and Rao (*196*) used *m*-nitrobenzoic acid or *o*-chlorobenzoic acid at pH 2.6 to 2.8 to separate thorium from uranium. In a later study benzoic acid (*324, 325*) was recommended for separation from uranium and from rare earth elements. Benzoic acid has been used for the determination of thorium and rare earth elements in alloys of magnesium. The latter cation introduces considerable difficulty in the determination as oxalate or hydroxide. Wengert, Walker, Louks and Stenger (*336*) precipitated thorium and zirconium by benzoic acid from slightly acid solutions of the magnesium alloy and subsequently isolated thorium by precipitation as the oxalate. Ammonium sebacate was used to separate the rare earth elements from the alkaline earth elements in the filtrate.

Sodium mercaptobenzothiazole in large excess was used by Spacu and Pirtea (*283*) to precipitate thorium. The white precipitate was dried at 105° to 110° C. and weighed. Various known methods for the determination of thorium in ores and its separation from rare earth elements were examined by Ingles (*135*). A detailed procedure was included. Rodden and Warf (*244*) reviewed the analytical chemistry of thorium and gave procedures for some 14 methods for gravimetric determination. Although satisfactory results could be obtained by weighing the 8-quinolinolate, the best methods involved the ignition to the oxide.

Přibil and Vorlićěk (*227*) extended further the applications of ethylenediaminetetraacetic acid in a procedure for the precipitation of ammonium uranate. Interference from some dozen and a half cations, including thorium and cerium, were thus eliminated. Salicylhydroxamic acid was used by Bhaduri (*27*) to precipitate uranium. The orange-colored precipitate was dried at 105° C. and weighed directly.

Hahn and Burros (*119*) successfully avoided the interference of phosphate in the determination of radioactive niobium. The addition of iodate ion to form a high iodate-phosphate ratio resulted in only slight coprecipitation of phosphate ion. The iodate was readily removed from the precipitate by washing with ammonium hydroxide and by ignition. Organic precipitants for trivalent and tetravalent plutonium were recorded by Patton (*208*).

ALKALI AND ALKALINE EARTH ELEMENTS

Sodium, Potassium, Rubidium, and Cesium. Sato and coworkers (*254–260*) published a number of papers dealing with the separation and determination of alkali metals. Potassium, rubidium, and cesium were precipitated as 2,2′,4,4′,6,6′-hexanitrodiphenylamine (hexyl) salts and separated from each other by selective extraction with various solvents (*254, 258*). Lithium and sodium in the filtrate were converted to chlorides and separated by treatment with hydrogen chloride–alcohol solution (*256*).

In a modified procedure, Sato (*259*) determined potassium by adding an excess of standardized hexyl reagent and subsequently weighing the excess of hexyl. According to Harrison (*121*), the precipitation of the triple acetate of sodium, was accompanied by that of potassium at temperatures below 4° to 6° C.

Kato and Okinaka (*142*) reduced the solubility of sodium dihydrogen pyroantimonate by using a saturated solution of the potassium salt. The determination of sodium in aluminum and its alloys by distillation in vacuum at 900° C. was discussed by McCamley, Scott, and Smart (*171*). The sodium zinc uranyl acetate method was applied to the distillate. Krivensov (*154*) introduced modifications of the cobaltinitrite method for the determination of small quantities of potassium.

Raff and Brotz (*231*) found that the sodium or lithium salt of tetraphenylboron could be used in a slightly acid medium for the determination of potassium in the absence of ammonium, rubidium, and cesium ions. The precipitate was stable on drying at 120°. Directions were included for the determination in the presence of alkaline earth elements. The method was simple and especially suitable for mineral analysis. Kohler (*148*) also used this method for the determination of potassium and ammonium under similar conditions. Subsequent to weighing, the mixed precipitates were dissolved in acetone, sodium hydroxide was added, and ammonia was distilled off. The isolated potassium tetraphenylboron was dried at 105° C.

A modification of these methods as applied to fertilizers was recorded by Berkhout (*24*). Used for smaller weights of potassium, the procedure involved precipitation in a slightly alkaline medium. Precipitation of the ammonium ion was avoided by the addition of formaldehyde and interference from calcium and magnesium was prevented by the use of ethylenediaminetetraacetic acid. While the method is superior to the perchloric method, the reagent is expensive and its recovery is advisable. Robinson (*242*) reviewed the analytical chemistry of potassium.

Calcium, Strontium, and Barium. Methyl oxalate was used by Gordon and Wroczynski (*105*) to precipitate calcium. The usual advantages of the internal production of the precipitating ion were realized. The standing period, required even with the urea method, was eliminated, the crystals of calcium oxalate were large, and a single precipitation served to separate 20 to 100 mg. of calcium from 100 mg. of magnesium. However, the authors did not preclude the possibility of insignificant contamination by magnesium.

Matsuo (*183*) also studied the influence of magnesium upon the precipitation of calcium oxalate. The rather surprising observation was made that for equal amounts of the two ions the precipitation should be carried out at room temperature and the precipitate kept for about 4 hours. To avoid inclusions of calcium oxide and carbonate during the conversion of calcium oxalate to sulfate Gautier and Renault (*99*) heated the precipitate prior to treatment with nitric and sulfuric acids.

For the determination of calcium in calcium oxalate Lazarev (*164*) obtained the most accurate and precise results by weighing as carbonate or sulfate. The calcium oxalate monohydrate and oxide methods produced high results. If dehydration was accomplished at temperatures higher than 100° C. the monohydrate was hygroscopic. Furthermore, the anhydrous oxalate recommended by Duval (*68*) as a weighing form was found unacceptable by Miller (*188*). This salt was also hydroscopic and as much as 0.7% error was noted in determining 90 mg. of calcium. Holth (*128*) rejected the monohydrate and oxide as weighing forms and accepted the carbonate.

The fact that it is difficult to fix the lowest temperature at which precipitated calcium carbonate can be calcined was discussed by Richer and Vallet (*239*). The decomposition temperature obtained by the thermobalance was affected by the mass and state of the sample and the rate of heating. The tungstate method for the determination of calcium in carbonate rocks was used by Povondra (*218*). Following the isolation of magnesium by a double 8-quinolinolate precipitation, calcium was precipitated at pH 8.0 to 8.5 by sodium tungstate.

Kobe and Motsch (*147*) developed a quantitative procedure for the determination of strontium in the presence of calcium from the known fact that the monobutyl ether of ethylene glycol selectively dissolved calcium nitrate from the anhydrous mixed nitrates of strontium and calcium. A correction curve was required and the authors discussed other disadvantages of the method. For the precipitation of strontium oxalate monohydrate Matsumoto (*182*) recommended a pH greater than 3 and introduced some changes in technique.

Wagner and Wuellner (*330*) used sulfamic acid for the precipitation of barium sulfate. This reagent had previously been recommended by Willard (*341*) for the separation of barium and calcium. The usual improved physical characteristics of the precipitate were observed.

An interesting method of precipitation of barium sulfate in the presence of lead ion was recorded by Přibil and Maričová (*224*). Ethylenediaminetetraacetic acid added to an ammonium acetate medium of pH 4.5 to 5.0, was used to eliminate interference from lead. There was included a useful method for sulfate determination in the presence of iron, chromium, and aluminum, which were complexed with ethylenediaminetetraacetic acid. If reprecipitation of barium sulfate was desirable an ammoniacal solution of the reagent dissolved the salt which was subsequently precipitated by acidifying with hydrochloric acid. These procedures will prove useful and their field of application will be extended.

Miura and Matsuo (*192*) studied the coprecipitation of nitrate ion with barium sulfate and concluded that most of the impurity appeared to be occluded in the adsorbed state on the inner surfaces of the barium sulfate. For the separation of barium from mixtures of barium sulfate and calcium sulfate, Castagnov and Larcebau (*45*) heated the mixture at 600° C. in the presence of orthophosphoric acid. Tsubaki (*309*) precipitated barium molybdate at pH 6.6 in the presence of calcium and strontium. Unohara (*316*) used the thermal balance to analyze without separation mixtures of the alkaline earth elements. The method involved the decomposition of the carbonates.

STEEL FORMING ELEMENTS

Titanium, Zirconium, and Hafnium. A promising approach to the separation of titanium from niobium and tantalum was reported by Atkinson, Steigman, and Hiskey (*10*). The chlorination was accomplished by heating the synthetic mixture of pentoxides at atmospheric pressure with octachloropropane and selectively distilling tetravalent titanium chloride. Anhydrous conditions were necessary and iron interfered, probably by decomposing the chlorinating reagent. The authors recorded that in one operation the concentration of titanium was reduced beyond spectroscopic detection.

Wernet (*338*) separated titanium from tantalum by precipitation as ammonium hexachlorotitanate(IV). For equal amounts of titanium(IV) oxide and tantalum(V) oxide less than 1% of titanium oxide remained with the tantalum. Přibil and Schneider (*225*) used ethylenediaminetetraacetic acid to eliminate interference from aluminum and iron in the precipitation of titanium by ammonia. Manganese and chromium coprecipitated. A procedure for the determination of titanium in bauxite was included. A procedure for the determination of titanium in permanent magnetic alloys by precipitation by cupferron was described by the British Standards Institute (*37*). Nogueira (*203*) applied known methods for the determination of titanium in the analysis of rutile and ilmenite.

Astanina and Ostroumov (*9*) found mandelic acid an effective reagent for the removal of zirconium from rare earth elements and molybdenum. Good results could be obtained by direct weighing. For quantities of zirconium of the order of 1 mg. or less, one or more days were required for complete precipitation.

Duval (*66*) found that the destruction of organic matter in the zirconium-mandelic precipitate resulted initially in a product which was slightly reduced. However, the spectra indicated pure zirconia. *p*-Bromomandelic acid was used by Hahn (*118*) to determine zirconium-hafnium ratios. The accuracy and precision of the method was ±0.5% for samples containing more than 10% of hafnium oxide. Determinations made in the presence of aluminum, iron, and titanium(IV) gave erratic results.

Stachtchenko and Duval (*285*) rejected the picric acid, potassium iodate, ammonium arsenate, and 8-quinolinol methods for the determination of zirconium. Aniline was the only reagent producing zirconium hydroxide; various other reagents produced zirconyl hydroxide. The authors recorded thermolysis curves for 17 zirconium precipitates. Several new reagents have been proposed for the precipitation of zirconium and its separation from cerite earths and certain bivalent and trivalent metals. In general the elements adjacent to zirconium in the Periodic Table interfered.

Cinnamic acid was used by Warlu and Rao (*333*); benzilic acid by Ventkataramaniah and Rao (*321*); and salicylic and phenoxyacetic acids by Sastry and Rao (*253*). Ventkataramaniah and Rao (*320*) used *m*-cresoxyacetic acid; titanium, tin(II), vanadium, and chromium contaminated the precipitate but were removed by reprecipitation; sulfate interfered. These authors (*331*) stated that while many bivalent and trivalent cations were not coprecipitated with zirconium by *m*-nitrobenzoic acid, double precipitations generally were required. Separations from thorium, hafnium, and thallium could not be made and tin(IV) interfered. Purushottam and Rao (*230*) recorded a modification of the tannin method for zirconium determinations.

Various processes for the separation of zirconium and hafnium have been published. Street (*286*) used a cationic ion-exchange resin, and Fujiwara (*89*) fused or sintered the pyrophosphate of hafnium and of zirconium with various mixtures. In the case of fusion with sodium sulfide or with magnesium carbonate plus ammonium chloride, hydrofluoric acid extracted about 90% of the zirconium. About 50% of the hafnium remained in the residue. An indirect method involving mixed precipitates to determine hafnium was also used (*88*). The pyrophosphates and oxides were successively formed and weighed. Methods such as this may be subject to large errors.

Loewenstein (*169*) studied the fractional precipitation of the phosphates in the presence of large amounts of sodium sulfate or sodium hydrogen sulfate. Hafnium was concentrated in the precipitate. Huffman and Beaufait (*131*) made extractions from a 2*M* perchloric acid medium with CF_3COCH_2COR (R = phenyl) in benzene. The zirconium was preferentially chelated and removed with the organic solvent. A triple extraction resulted in a recovery of hafnium contaminated by 0.4% zirconium.

Vanadium, Niobium, and Tantalum. The determination of vanadium by diantipyrylphenylmethane was described by Gusev, Beǐles, and Sokolova (*113*). The precipitate could be dried and weighed, ignited to the pentavalent oxide, or a volumetric procedure could be applied. Iron interfered. Tsubaki and Hara (*311*) separated tetravalent and pentavalent vanadium in an ammonium acetate medium by precipitating the former at pH 7.0 by ammonium hydrogen phosphate and the latter in acetic acid medium at pH 5.5 to 6.0 by 8-quinolinol.

Atkinson, Steigman, and Hiskey (*10*) dealt with the present unsatisfactory state of analysis for tantalum and niobium. A contributing factor was the colloidal character of aqueous solutions of their compounds. The authors emphasize a survey originally recorded by Slavin, Pinto, and Pinto (*277*) in which comparative analyses of two tantaloniobate ores were made by eight different workers employing five methods. The results revealed a rather striking lack of agreement.

Doan and Duval (*62*) determined pyrolysis curves for six niobium precipitates. None possessed any distinctive advantage and none was recommended for automatic determination. For tantalum, these authors (*61*) examined four methods and gave preference to precipitation by tartaric acid. *Morin and quercetin* were used by Tomíček and Holeček (*306*) to precipitate a red compound with niobium and an orange compound with tantalum. The determination of each element involved fusion of the oxides with potassium hydrogen sulfate and subsequent treatment with ammonium oxalate. A methyl alcohol solution of the reagent was used, and the precipitate, after standing overnight, was ignited to the oxide.

Hayashi (*124*) recorded the optimum ignition temperatures of tannin complexes of niobium and tantalum precipitated alone or in the presence of various alkaloids. A procedure for the determination of niobium in high-alloy steels free of tungsten was published by Golubtsova (*102*). The alloys were treated with hydrochloric and nitric acids. The evaporated residue was leached with a hydrochloric acid solution and, following the addition of macerated paper, the oxides of niobium and silicon were separated by filtration. The silica was removed in the conventional manner. Variations in the procedure were used if titanium or vanadium were present.

Popova and Platonova (*217*) provided a method for the determination of niobium carbide in steels. Ku and Chien (*156*) discussed the determination of earth acids in wolframite by fusion with caustic soda. Milner and Wood (*190*) separated tantalum and niobium from uranium by extraction of the fluorides of tantalum and niobium from aqueous solution into methyl ethyl ketone.

Molybdenum and Tungsten. Přibil and Sedlář (*226*) used ethylenediaminetetraacetic acid to prevent interference from various metal ions in the determination of molybdenum by 8-quinolinol. Procedures were described for molybdenum in the presence of cobalt, manganese, and nickel; copper; iron; uranium; and Group I metals. 8-Quinolinol was also used in the presence of ethylenediaminetetraacetic acid and ammonium acetate to precipitate tungsten, molybdenum, and vanadium. Other cations remained in solution. Various specific procedures were recorded—e.g., determination of tungsten in the presence of copper, iron, aluminum, chromium, uranium, cobalt, manganese, and nickel; simultaneous estimation of tungsten with uranium, copper, or cobalt; and the determination of tungsten, iron, and cobalt and of tungsten, uranium, and cobalt.

Garcia (*98*) published procedures for the determination of molybdenum in steels by 8-quinolinol in the absence or presence of vanadium or tungsten. Sudô (*288*) used sodium polysulfide satisfactorily for the determination of molybdenum in iron and steel samples. The application of ammonium and potassium polysulfides was also investigated.

For iron and low-alloy steels containing up to 0.5% tungsten, Craven (*54*) precipitated molybdenum(VI) sulfide by decomposition of an alkali thiomolybdate with dilute acids. Tartrate was used to overcome interference from tungsten and separation from iron was accomplished by the formation of the α-benzoinoxime complex. For the determination of molybdenum in these low alloy steels a standard procedure was recorded (*41*) which involved similar technique.

An improved molybdenum sulfide precipitation was devised by Rây (*238*). Ammonium thiosulfate solution was added to the hydrochloric acid solution of molybdenum followed by addition of an acidified solution of sodium hypophosphite. The sulfide was ignited at 550° to 575° C. This new procedure avoided both gassing and pressure precipitation. Methods were provided for the determination of molybdenum in steels and in ferromolybdenum. Factors affecting the accuracy of barium molybdate precipitations were discussed by Liang and Hsu (*166*). The precipitate was ignited at 300° to 900° C. Dupuis and Duval (*64*) recommended ignition above 320° C.

Thermolysis curves of tungsten precipitates were recorded by de Clerq and Duval (*53*). Precipitations by calcium, cadmium, and lead and by cumidine were recommended. No organic complexes stable at low temperatures were found; the formula given for the 8-quinolinolate was questioned. Methods using the blue oxide were considered unsatisfactory. Either *p*- or *o*-toluquinaldine was used by Golubtsova and Shemyakin (*103*) to determine tungsten in steels. In acid solutions titanium, iron, and molybdenum did not interfere. Molybdenum was precipitated from the filtrate by β-naphthoquinoline.

Belcher and Nutten (*22*) found that 1-amino-4-(*p*-aminophenyl)naphthalene in $0.7N$ hydrochloric acid precipitated tungsten but not molybdenum. In neutral solution these metals were precipitated by benzidine, diphenyline (2,4′-biphenyldiamine), and 4,4′-diaminostilbene. With increasing concentrations of hydrochloric acid the precipitation of tungsten was incomplete.

Chrysoidine R and Bismark Brown were used by Liang and Chang (*165*) to replace cinchonine for the precipitation of tungsten(VI) oxide. Ku and Wang (*157*) improved the physical characteristics of tungstic acid precipitate by employing slow decomposition of the chlorotungstate or oxalatotungstate complexes in acid media.

Chromium, Manganese, and Rhenium. Penchev and coworkers have extended their researches on the determination of chromium. The conditions affecting the accuracy of the mercurous chromate precipitation were investigated (*210*). Losses in acidic solutions depended on the nature of the acid and ranged from 0.3 to 2.5%. The chromium(III) hydroxide method was also examined (*209*). Ignition at 960° to 980° C. resulted in a positive error which varied with the nature of the anion, and was especially great in the presence of sulfate. Dehydration at 1100° to 1150° C. gave relatively good results. These data corresponded roughly to those recorded in the authors' earlier publications. Dupuis and Duval (*65*), who determined safe minimum heating temperatures for chromium hydroxide obtained by some dozen methods, recorded 812° C. for the hydroxide obtained by the addition of aqueous ammonia to chromium(III) salt. The discrepancy between the values obtained by these authors illustrates one of the difficulties in the interpretation of pyrolysis curves because of the presence of impurities.

Spacu and Lupan (*280*) separated divalent manganese ion from iron and aluminum by precipitation as a thiocyanate from a cold solution containing tartaric acid and excess pyridine. The purified precipitate of tetrapyridinomanganese(II) thiocyanate was dried and weighed. Improvements in the technique of determining manganese as sulfate and phosphate were described by Jovanović and Jovanović (*137*). Calcination of the pyrophosphate required 10 minutes at 900° C.; however, manganese could be determined accurately by direct weighing of ammonium manganese phosphate monohydrate.

Tribalat and Duval (*308*) recommended the tetraphenylarsonium perrhenate method for the automatic determination of rhenium. Geilmann and Bode (*100*) described various procedures for the separation of rhenium from metals of the hydrogen sulfide–acid group; these could be separated en masse by hydrogen sulfide in 5–6 *N* hydrochloric acid. In a second investigation these authors (*101*) separated rhenium from arsenic, antimony, tin, gold, germanium, selenium, and tellurium. Although the separations described are not new in character they merit detailed examination by the chemist who is interested in the analytical chemistry of rhenium.

Iron, Cobalt, and Nickel. Duval and Xuong (*70*) proposed a separation of iron and titanium based on their discovery that the cupferronate of iron remained stable up to 90° C. while that of titanium decomposed at 40° C. The authors recorded pyrolysis curves for 22 iron precipitates. The following reagents were considered unsatisfactory: ammonium sulfide, 5,7-dichloro-8-quinolinol, and sodium benzenesulfinate.

Gandolfo (*96*) separated iron from aluminum by treatment of the sulfuric acid solution with potassium iodide to form ferroferrite which was subsequently precipitated as the hydroxide by addition of sodium hydroxide. Norwitz and Tudor (*204*) discussed the relationship of the proportions of ammonium hydroxide to the interference of phosphate in the precipitation of iron hydroxide.

Sierra and Martinez (*273*, *275*), studied the optimum conditions for the precipitation of cobalt hexathiocyanate mercurate. The best results were obtained by precipitation by 25% sodium thiocyanate at 0 to 10° C. in the presence of glycerol and ethanol. The authors (*274*) also recorded the effects of sulfuric, nitric, orthophosphoric, and citric acids and their salts. The method was unsatisfactory in the presence of hydrochloric or tartaric acids. Young and Simpson (*346*) recorded a method for the differentiation of cobalt oxides. Glacial acetic acid selectively extracted cobalt(II) oxide.

Terent'ev and Rukhadze (*303*) modified the usual procedure for the precipitation of nickel by salicylalamine. Precipitation began at pH 8 and was completed at pH 9. Kuraš and Ruzicka (*159*) analyzed the precipitates of nickel dimethylglyoxime obtained in alkaline solutions containing bromine. For the determination of large amounts of nickel, Bickerdike (*28*) arranged for the slow precipitation of nickel dimethylglyoxime. The crystals were coarse and did not stick to the glass.

Moraine (*193*) recorded a procedure for the determination of nickel in cyanide solutions. Prior to the addition of excess ammonia the acidity of the solution was controlled by titration with silver nitrate in the presence of ammonium chloride. Reprecipitation in the presence of tartaric acid was required and nickel was determined finally by ignition to nickel(II) oxide. A method for the determination of nickel in the presence of aluminum, chromium, manganese, iron, and zinc was described by Chuĭko (*50*). Following precipitation by potassium ferricyanide and subsequent addition of sodium hydroxide solution, the hydroxides of manganese, cobalt, iron, and nickel were treated to separate manganese(IV) oxide, which contained iron and nickel. The final stages of concentration of nickel involved solvent extraction of nickel dimethylglyoxime with chloroform.

1,2-Cycloheptenedionedioxime, as a reagent for nickel, continues to receive well deserved attention. Longo (*170*) studied the effect of various ions on the accuracy of the method. Interference from iron as well as from aluminum and chromium was eliminated by tartrate. In the presence of large amounts of the complexing reagent, errors of less than 1% were realized with samples of 2 to 10 mg. Goto and Otaka (*107*) discussed the determination of nickel in high-cobalt alloys and in cobalt. The methods used depended upon the proportions of nickel.

NONFERROUS ELEMENTS

Copper, Cadmium, Zinc, Mercury, and Bismuth. A large number of procedures for the separation of copper from cadmium have been published. Hirata (*125*) precipitated copper in the presence of cadmium by adding salicylaldehyde-ethylenediimine to an ammoniacal solution. Cadmium was removed from the filtrate by 8-quinolinol. Both precipitates were weighed after drying.

Raju and Neelakantam (*233*) used resacetophenone (2,4-dihydroxyacetophenone) oxime in an acetic acid medium to precipitate copper resacetophenone oxime which was dried at 120° C. and weighed. These authors (*236*) stated that the dithiocarbamidohydrazine method for copper and cadmium described by Gupta and Charkrabartty (*110*) was inaccurate and lacked precision. Improved procedures involved burning the complex and determining copper as the oxide or iodometrically. In reply Gupta and Srinivasan (*111*) acknowledged that the precipitation of the copper complex was incomplete to the extent of less than 1%.

Calzolari (*44*) used dimethyldithiohydantoin. The copper salt could be precipitated in both acid and ammoniacal media, and of about 20 cations examined only silver and mercury(II) interfered. Directions were given for the removal of this interference. Krugovoĭ (*155*) used potassium iodide in a slightly acid solution. Cadmium in the filtrate was precipitated as the sulfide. Majumdar and De (*176*) precipitated copper at pH 1.15 to 1.85 by 5,6-benzoquinaldic acid, then precipitated cadmium in the filtrate at pH 3.12 to 3.85. Kumov (*158*) used diantipyryl-*o*-hydroxyphenylmethane in acid solution containing potassium bromide which precipitated cadmium but not copper and zinc; similarly diantipyrylmethane may be used (*347*).

Ubaldini and Guerrieri (*313*) used anthracenesuccinic acid for the determination of cadmium and for its separation from copper. Spacu and Cristea-Gheorghiu (*278*) reduced copper by sulfurous acid solution and precipitated copper(I) thiocyanate which was dried and weighed. The filtrate was boiled to remove sulfur dioxide, and then treated with excess pyridine and ammonium thiocyanate. The precipitate of dipyridinocadmium thiocyanate was dried and weighed. Similarly Spacu and Cristea-Gheorghiu (*279*) separated and determined copper and zinc by ammonium thiocyanate.

Belcher and West (*23*) determined the conditions affecting quantitative precipitation of copper(I) thiocyanate. Ferrous ammonium sulfate was used as a reducing reagent and the usual drying temperature of 110° C. was used. Marin and Duval (*180*) found that the thermolysis curve for copper(I) thiocyanate rose very slightly up to about 300° C. The increase in weight amounted to about one in one hundred and fifty. At about 950° C. copper(II) oxide was obtained. The authors determined curves for 67 precipitates. All but 12 of these methods were considered unsatisfactory. New methods were proposed based on precipitation by cupferron and neocupferron which produced complexes stable up to 100° C.

Gagliardi and Pilz (*93*) used trithiocarbonic acid to precipitate copper(II) sulfide. Acid concentrations of 0.1 to 6.0*N* were suitable and the precipitate was easily filtered and washed. For the separation of copper from bismuth, antimony and tin, Spacu and Pirtea (*281*) used tartaric acid as the complexing reagent. Copper was precipitated as dipyridine copper(II) thiocyanate.

Walter and Freiser (*331*) developed an interesting method for the determination of cadmium which appears to be highly selective. When precipitations were made by 2-(*o*-hydroxylphenyl)benzoxazole at pH 10.5 in the presence of tartrate most interferences were eliminated, although nickel and cobalt interfered if present in amounts greater than 20 mg. Copper was removed by prior precipitation by the same reagent in a medium of higher acidity. The cadmium precipitate was weighed after drying at 130° to 140° C. Vinogradova (*328*) investigated the effect of various anions on the pH at which cadmium hydroxide was precipitated. The final precipitate always proved pure cadmium hydroxide.

In a publication worthy of attention Vance and Borup (*318*) record the results of investigating by tracer technique the completeness of various well known methods of separating and precipitating zinc. The phosphate method was modified to advantage and good results were obtained with zinc ammonium phosphate dried at 100° C. or with the pyrophosphate heated at 500° to 600° C. The homogeneous precipitation by ethyl oxalate was entirely comparable in effectiveness to the phosphate method. Precipitations by 8-quinolinol and anthranilic acid were also examined. With the former reagent, heating to the anhydrous precipitate at 125° C. was preferred to obtaining the hemihydrate at 100° C. An empirical factor was required. With anthranilic acid the removal of zinc was complete but the composition of the precipitate varied with the temperature of the solution. Precipitation by sulfide from a cold sulfate-bisulfate buffer in the presence of iron, nickel, manganese, and aluminum was discussed in some detail.

A British Standards Institute method for the determination of zinc in aluminum and its alloys has been recorded (*40*). Following the separation of silicon and copper, zinc was precipitated as a sulfide, in a tartaric acid–formic acid medium. The sulfide was extracted with acid, lead was removed as the sulfate, and zinc mercuric thiocyanate was precipitated, dried, and weighed. The method was recommended for zinc contents between 0.10 and 6%. For lower contents the precipitation procedure was followed by a volumetric determination.

Pilz (*214*) preferred precipitation of zinc sulfide by trithiocarbonic acid to precipitation by hydrogen sulfide. Filter paper pulp improved filtration and the sulfide could be determined volumetrically or ignited to the oxide. The gravimetric method yielded slightly better results. Takagi, Nakano, and Hirano (*294*) found that aqua regia did not oxidize zinc sulfide to sulfate. Oxidation in a sealed tube with hydrochloric and nitric acids was satisfactory.

The pyrolysis curve of zinc mercuric thiocyanate as obtained by de Clercq and Duval (*52*) indicated safe drying temperatures up to 120° C; between 120° and 270° C. there was observed a gain in weight of about 0.3%. The authors recorded eight reagents for the automatic determination of zinc. Optimum concentration and acidity for the precipitation of zinc phosphate were described by Matsuo (*184*). A pH of 6.8 to 7.2 was recommended. For the isolation of various zinc compounds in zinciferous minerals, Freney, Collée, and Grodent (*86*) used selective solvents and applied standard methods to the extracts.

Hall and Smith (*120*) used 1,10-phenanthroline ferrous sulfate in potassium bromide solution at a pH of about 5 to precipitate dark red crystalline ferroin tribromomercuriate. The precipitate was washed with hydrobromic acid solution, dried at 110° C., and weighed. The method was suitable only for weights of mercury ranging from about 1 to 60 mg. Free mineral acids interfered. The causes of interference from various cations and anions were also discussed.

Phenylboric acid was used by Holzbecher (*129*) to precipitate mercury as diphenylmercury. Depending upon the identity of the anions, solutions of sodium acetate or ammonium hydroxide were used to buffer the precipitating medium. The precipitate was dried at 70° C. and weighed in a vacuum. Sedivec (*270*) recorded a useful method for the precipitation of mercury(II) by mercaptophenylthiadiazole in a medium containing ethylenediaminetetraacetic acid. With the exception of silver there was no interference from the cations which commonly interfere. The precipitate was dried at 105° C. and weighed directly.

Walter and Freiser (*332*) used 2-(*o*-hydroxyphenyl)-benzimidazole which avoided the interference of many cations including silver but not iron(III) when the latter was present in amounts greater than a few milligrams. The purified precipitate could be weighed directly or a volumetric adaptation could be used. Sakuraba (*250, 251*) used silver ion to initiate the reduction of mercury(II) chloride by phosphorus acid or hypophosphite. Flaschka and Jakoblevich (*82*) obtained precision but not accuracy from the thioacetamide precipitation of mercuric sulfide in an acid medium. Duval and Xuong (*71*) recorded the pyrolysis curves for 22 mercury precipitates. The stability of the mercury(II) sulfides differed according to the precipitating reagent used.

Panchout and Duval (*207*) examined the procedures available for the gravimetric determination of bismuth and concluded that the phenyldithiobiazolonethiol method as described by Majumdar (*175*) was the best available. In addition the phenylarsonic method also developed by Majumdar (*174*) and the thionalide procedure were recommended. Fifteen reagents were found suitable for automatic determinations. Fourteen known reagents were considered unsuitable. An interesting method proposed by Přibil and Čuta (*222*) for the separation of bismuth from associated metals involved the relative instability of the complex formed with ethylenediaminetetraacetic acid. The latter could be removed by addition of a calcium salt. A procedure for the determination of bismuth in lead alloys was included.

Thallium. Forchheimer and Epple (*84*) discussed the precipitation of thallium(I) from perchloric acid solutions containing thallium(III), iron(II) or -(III), nickel, copper, aluminum, manganese, and other elements which in previously published methods required complexing reagents. These complexing reagents interfered by either oxidizing the thallous or reducing the thallic salt. The new separation of thallous ion was accomplished by precipitating the dichromate, which was subsequently converted to the chromate by alkaline cyanide solution, after washing free of other cations. Under the conditions described the method was satisfactory for weights of thallium(I) of less than 50 mg., or larger weights in the absence of thallium(III).

Přibil and Zábranský (*228*) used ethylenediaminetetraacetic acid to eliminate interference from lead, copper, bismuth, and iron in the precipitation of thallium iodide. Subsequent to the concentration of thallium, Efremov (*73*) used the iodide or chromate methods for its determination in chlorides of marine origin. Murakami (*195*) determined thallium in flue dust by precipitating $Co(NH_3)_6TlCl_6$. There were no interferences from copper, iron, zinc, lead, and other commonly associated elements. A review of the methods recorded from 1940–1950 for the detection and determination of thallium was published by Anderson (*7*). Although reference is made to most of the commonly used gravimetric reagents, no critical evaluation is included.

Germanium, Tin, and Lead. Bevillard and coworkers (*26, 300–302*) listed some 18 organic reagents for the precipitation of germanium. They drew the conclusion that reagents must possess two functional phenol groupings in ortho positions, and in the para position to one of these there must be a group which favors ionization of the opposed phenol group. Directions were given for precipitation of germanium by 3,4-dihydroxyazobenzene (*302*). The minimum concentrations of germanium required to produce precipitation by six different reagents were also recorded (*301*). Analytical methods for the determination of germanium were reviewed by Krause and Johnson (*149*). A section deals with gravimetric precipitants.

A useful method for the precipitation of tin was described by Ryan and Lutwick (*248*). The reagent *N*-benzoylphenylhydroxylamine was used in solutions containing 1 to 8% hydrochloric acid. Because there were no interferences from copper, lead, or zinc the method was applicable to brasses. The purified precipitate $(C_{13}H_{11}O_2N)_2SnCl_2$ was dried at 110° C. The homogeneous precipitation of tin in ammonium sulfate media by hydrolysis with urea was discussed by Willard and Gordon (*342*). Although the precipitate of "basic stannic sulfate" possessed excellent physical features it was rejected as an analytical method for tin because of serious coprecipitation of other metals and tenacious adherence to beaker walls. However, the precipitate could be applied as a carrier in the study of coprecipitation phenomena.

Simonsen and Booth (*276*) provided further interesting data on the conditions which affected the contamination of precipitated tin(IV) sulfide by cobalt. Contrary to previous practice the authors used varying concentrations of dilute acids, and such factors as concentration of cobalt and tin, and period of aging, were held as constant as possible. However, the acidities used resulted in the presence of metastannic acid as a dissolved constituent and required the addition of potassium chloride to avoid peptization of tin sulfide. A partial explanation is offered for the observed data.

Bagshawe (*14*) determined tin in ferrotungsten and tungsten metal by precipitation of the sulfide after complexing tungsten with citric acid or removal of tungsten by hydrolytic precipitation. Besson and Budenz (*25*) determined tin in bronzes containing silicon by coprecipitation of the hydrated dioxides of both elements and subsequently eliminating tin as the tetraiodide.

Majumdar and Sarma (*177*) used benzenearsonic acid to precipitate lead from a solution at pH 6.8 to 7.4. The lead content of the precipitate was about 1% less than theoretical. Sodium, potassium, and calcium coprecipitated. The homogeneous precipitation of lead sulfate was accomplished by Elving and Zook (*75*). Aqueous methanol containing dimethyl sulfate was used as the hydrolyzing medium and the usual improvements in crystal form were observed. The various factors affecting precipitation were studied and interesting data concerning interferences from iron and aluminum were included. An excess of nitrate ion increased the solubility of lead sulfate.

The coprecipitation of nitrate ion with lead sulfate was discussed by Kobayashi, Murai, and Otani (*146*). Precipitation was accomplished by adding potassium sulfate to lead nitrate. Tananaev and Mizetskaya (*297*) studied the systems lead sulfate–sulfuric acid–water and lead sulfate–lead nitrate–water and dealt with the explanation for the solubility of lead sulfate in sulfuric acid. Because of this solubility effect they preferred to precipitate lead as $K_2SO_4.PbSO_4$. Guthrie and Nance (*114*) separated lead from silver by addition of chromate ion to the appearance of silver chromate. Addition of excess ammonia dissolved the silver salt and lead was precipitated as $PbO.PbCrO_4$.

For the precipitation of lead as normal phosphate Liang and Lu (*167*) recommended the pH range of 6.5 to 10.0. Other optimum conditions were described. Kallman (*138*) extended the application of *n*-butyl alcohol–hydrogen chloride to the separation of lead and bismuth. Only a single separation was required. Bismuth could be determined in the filtrate as bismuthyl chloride by applying an empirical factor to the precipitate. There was interference from sodium, potassium, barium, strontium, and silver. Rodewald (*245*) recorded a procedure for the determination of small quantities of lead in chromic oxide. Standard methods of separation and precipitation were used. For the determination of lead in steels, Rosi (*247*) avoided the difficulties incident to the rather critical optimum acidity by precipitating lead sulfide in a tartaric acid medium.

Antimony, Arsenic, Selenium, and Tellurium. For the determination of arsenic in alkaline arsenite, Romano (*246*) used potassium xanthate in an acetic acid medium. The precipitate was weighed directly. Trithiocarbonic acid, which has been used by Pilz and coworkers for the determination of zinc, copper, and molybdenum, is now recommended by Gagliardi and Pilz (*94*) for the precipitation of antimony(III) sulfide. The usual orange and black modifications were obtained, but with the latter improved accuracy was realized. Compared to the hydrogen sulfide method the proposed procedure resulted in more rapid precipitation and the odor was less intense. The orange and black sulfides may also be formed by precipitation by thioformamide (*198*).

For the determination of antimony, Márquez (*181*) used powdered aluminum to convert orange antimony(III) sulfide to the black sulfide which was dried and weighed. Belcher and Gibbons (*21*) precipitated antimony as dichlorobisethylenediaminocobaltic hexachlorostibnate. Lead interfered.

Mendoza (*187*) used thiosemicarbazide in acid solution to precipitate selenium. Methods of avoiding interferences from some 10 chemicals, including tellurite ion, were described. Fidler (*78*) used weakly alkaline conditions for precipitation by glucose of the crystalline modification of selenium, which was dried at 105° C.

The estimation of selenium by precipitation of mercury(II) selenite was discussed by Deshmukh and Sankaranarayanan (*57*). The amorphous white precipitate obtained at pH 4 to 10 could be weighed after drying at 100° C. Silver interfered. Goto and coworkers (*106, 108*) recorded procedures for the determination of selenium and tellurium. Following dissolution of these elements in perchloric acid, selenium was precipitated by sulfur dioxide in a medium 9*N* in hydrochloric acid. Tellurium was similarly precipitated from the filtrate diluted to 2 to 4*N*. The effects of perchloric acid on the precipitation were discussed (*108*).

Duval and Doan (*69*) recorded pyrolysis curves for lead selenate and for precipitated selenium obtained by four methods. For automatic determinations, tin(II) chloride and lead nitrate are recommended reagents. For the determination of selenium in stainless steels, Mott (*194*) used a mixture of mineral acids including hydrofluoric and perchloric to effect dissolution. Selenium was precipitated by hydroxylamine hydrochloride. The precipitate was dried, weighed, and ignited; the difference was accepted as the weight of selenium.

Bode (*31*) used tetraphenylarsonium chloride to precipitate tellurium in the presence of selenium. The precipitate, $(C_6H_5)_4As_2TeCl_2$ obtained in the presence of 5*N* hydrochloric acid could be dried at about 100° C. and weighed. A considerable number of anions and cations interfered. Doan and Duval (*60*) concluded that no acceptable gravimetric method for tellurium was available; of those recorded, precipitation by vanadyl sulfate was the best.

RARE EARTH ELEMENTS

Scandium, Lanthanum, and Cerium. Beck (*19*) stated that scandium could be precipitated from acid solutions by adenosinetriphosphate and by aneurine and inosital pyrophosphates. A procedure for the determination of scandium by 8-quinolinol was described by Pokras and Bernays (*216*). They investigated the effect of temperature, quantities of reagent and buffer, pH of solution, temperature of ignition, size of sample, and use of Aerosol. The procedure adopted involved the removal of rare earth elements and aluminum, addition of Aerosol and 8-quinolinol, and buffering so that the final pH of the solution was 8.5. The precipitate was weighed after drying at 100° to 110° C.

The extreme insolubility of lanthanum ethylenediaminetetraacetate was noted by Brintzinger, Thiele, and Muller (*36*). They proposed to use this compound for the separation and determination of lanthanum. Fitch and Russell (*80*) suggested that specific eluting reagents for isolating various members of the lanthanide series might be found among substituted iminodiacetic acids. They used hydrazine diacetic acid to separate all but lanthanum from a mixture of rare earth elements adsorbed on a cation exchange bed. Lanthanum was subsequently extracted by 0.5% of the acid with 1.5% ammonium acetate at pH 5.5, precipitated as the oxalate, and ignited to the oxide. Preliminary to the adsorption, cerium was advantageously removed by chemical methods. Misumi (*191*) used 8-quinolinol to precipitate lanthanum at a minimum pH of 7.1 and cerium(III) at a minimum pH of 9.4. The solutions were buffered by ammonium succinate or tartrate.

Johnson (*136*) recorded a procedure for determining cerium in steels. The high-chromium steels were dissolved in sulfuric acid and sodium peroxide was added. The precipitate was redissolved and the cerium isolated by an oxalate precipitation.

NOBLE ELEMENTS

Silver, Gold, Palladium, Platinum, Osmium, and Iridium. The wide applications of mercaptobenzothiazole were extended to the precipitation of silver. Ubaldini and Nebbia (*314*) used an ammoniacal solution and weighed the light-insensitive precipitate after drying at 105° to 110° C. In acid solution the precipitate must be ignited. Sandell and Neumayer (*252*) determined the solubility product for silver *p*-diethylaminobenzylidinerhodanate. The losses of silver occurring during fire assay were discussed by Chopin (*49*) who found that error arising from the vapor pressure of silver was negligible compared to the inherent errors of the method.

Champ, Fauconnier, and Duval (*47*) recommended citarin, hydroquinone, and benzenethiol for the automatic determination of gold. Duval (*66*) suggested an examination of derivatives of benzenethiol as precipitants for gold. Because of the favorable weight factor the author preferred direct weighing of aurous benzenethiolate to subsequent ignition with its accompanying objectionable odor. The authors who first recorded thiophenol as a reagent for gold (*55*) disapproved of the method because of the objectionable odor and the instability of the precipitant.

According to Watanabe (*334*) the deleterious effect of tellurium on the recovery of gold by cupellation could be minimized by using more than 25 grams of lead for 1 assay ton of ore. Ripan and Paladi (*240*) investigated the effects of tellurium on gold recovery by fire assay. At certain concentrations of tellurium all of the gold was lost to the cupel. Losses could be minimized by increasing the proportion of flux or by removing the tellurium with nitric acid.

Pyrolysis curves for palladium precipitates were recorded by Champ, Fauconnier, and Duval (*48*). Oximes and *o*-phenanthroline were preferred reagents. The authors considered ignition of the palladium dimethylglyoxime and subsequent reduction of the oxide in hydrogen inferior to direct weighing of the organometallic compound. Their reference to the latter method as a new weighing form obviously was not intended to indicate a discovery arising out of their work. The pyrolysis curve for this compound reveals rapid decomposition between 195° and 259° C. Data have been recorded in the literature suggesting that a slight loss of palladium occurs prior to or at the temperature of ignition. Perhaps the Chevenard balance could provide the answer to this phenomenon.

Gagliardi and Pietsch (*91*) used thioformamide in hot solution to precipitate palladium sulfide. Saini (*249*) precipitated divalent palladium hydroxide by adding arciflavine to a sodium acetate medium. The accuracy of recovery was not good and various associated cations interfered. Ayres and Tuffly (*12*) precipitated palladium by dithiooxamide. Platinum and gold also formed precipitates.

No specific reagent for the gravimetric determination of platinum has ever been recorded. Naito (*200*) used phenylthiosemicarbazide to precipitate platinum. Bode (*30*) used tetraphenylarsonium bromide. The orange precipitate was dried at 110° C. and weighed. Ubaldini and Nebbia (*315*) concluded their review of the methods of analysis of commercial platinum.

A new approach to the determination of osmium was used by Musil and Pietsch (*199*). These authors dry-distilled octovalent osmium oxide by heating the sample in a stream of oxygen and weighing the distillate collected in potassium hydroxide. It is difficult to conceive of instances when this method could be applied. In its natural state osmium forms part of an alloy which only very infrequently permits any formation of osmium tetraoxide by direct oxidation. Consequently from those occurrences now known the method is not applicable. For aqueous solutions of osmium the present procedures are incomparably superior. Perhaps this new method may find some use in the analysis of mixed precipitates.

The efficiency of the recovery of osmium by collection in lead was discussed by Allan and Beamish (*6*). Measured by means of synthetic samples the loss of osmium may reach 6%. There is considerable significance in the loss of osmium to the slag. During the investigation this loss was deliberately accentuated by a fusion prior to the addition of the lead oxide. The data obtained could mean that at least some of the platinum metals may occur in forms which prevent complete recovery of the metal by the usual fire assay processes.

A similar investigation was made of fire assay losses of iridium (*15*). As might be expected, since iridium does not alloy with lead, re-assay of the slags is usually required. For copper or nickel ores requiring high contents of litharge the losses of iridium were serious. A high silver-iridium ratio did not prevent losses during cupellation. In general cupellation is not acceptable where good accuracy is required because of the high mechanical losses. In the case of osmium the cupellation process is inadmissible since the volatile osmium(VIII) oxide is formed.

The gravimetric determination of iridium and the separation of iridium from lead which remained after the acid parting of a fire assay button were discussed by Barefoot, McDonnell, and Beamish (*16*). Two methods were used. In one the iridium was complexed with nitrite and lead was removed as the phosphate. The second procedure involved the precipitation of iridium in acetate solution by mercaptobenzothiazole. Gagliardi and Pietsch (*92*) used thioformamide for the precipitation of iridium and the separation of palladium from iridium. The time for precipitation of the sulfide is lengthy, precipitation is incomplete, and the separation is not clean. The method has little to recommend it.

NONMETALLIC ELEMENTS

Carbon and Silicon. Yebra Montagut and Rich (*345*) separated amorphous carbon from graphite carbon by removal of the former with sulfuric acid containing potassium sulfate. Baron (*17*) determined free carbon in silicon carbide by heating the sample on a Chevenard balance at 725° ± 25° C. At 830° C. silicon carbide was oxidized to form silicon dioxide and carbon monoxide. When oxygen or chromic acid is used to oxidize boron carbide the rate of oxidation at constant temperature is constant and differs from the rate of oxidation of free carbon. Meerson and Samsonov (*185*) measured the rate of oxidation of the sample to be oxidized and used the known rate of oxidation of boron carbide to determine the free carbon.

Talvitie (*295*) separated silicates from quartz by treating the finely ground sample with phosphoric acid to form pyrophosphoric acid which selectively removed the silicates. The method was simple, requiring a minimum of laboratory equipment and the results compared favorably with sulfuric acid and X-ray diffraction procedures; however, there was the disadvantage that efficiency of extraction of silicates varied with the character of the equipment and of the sample.

For the determination of silicon in niobium-tungsten alloys Pen'Kova and Yakovlev (*211*) recommended complexing the metals with ammonium oxalate. Directions were given for decomposing ferrotungsten samples and subsequently determining silica. For the determination of silicon in slags containing fluorine Lamure (*162*) used orthoboric acid in perchloric acid medium to volatilize fluorine. The silica was dried at 100° C. and ignited at 950° C. A similar procedure was recommended by Tsubaki and Hara (*310*). In this case excess boric acid was removed by evaporation with methyl alcohol. Lamure and Henriet (*163*) dehydrated with acetic anhydride following the usual hydrochloric acid treatment of residues.

According to van der Weel (*335*) a precipitate of silica could be prepared for efficient filtration without the addition of colloids or ammonium nitrate or chloride. Schütz and Antoni (*268*) used specially designed crucibles and equipment to speed up control analyses of silicates. Baron (*18*) reviewed methods for the determination of silica in specific ferrous minerals.

Nitrogen, Phosphorus, Sulfur, and Fluorine. Duval recorded pyrolysis curves for precipitates used for the determination of cyanogen derivatives (*67*) and for nitrogen derivatives (*72*). Dicyclohexylthallic ion was used by Hartmann and Bäthge (*123*) for the gravimetric or volumetric determination of nitrate.

Schleicher and Bochem (*267*) compared the reliability and sensitivity of nine methods for the determination of phosphoric acid in aqueous solutions. A specified gravimetric procedure was considered to be the most reliable and a colorimetric method the most sensitive. The separation of ammonium magnesium phosphate from various cations which form insoluble phosphates was accomplished by Přibil and Jelínkova (*223*) through the use of ethylenediaminetetraacetic acid or Tiron (pyrocatechol-3,5-disulfonic acid).

Dewald and Schmidt (*59*) used a modified barium chloride method for the separation of hexametaphosphate from orthophosphate. The former was precipitated in acid medium and the latter was isolated from the basic filtrate; the precipitated orthophosphate was dissolved, converted to molybdate, and the phosphorus determined as magnesium pyrophosphate. For the precipitation of silver phosphate Ubaldini and Guerrieri (*312*) neutralized the solution by addition of sodium nitrite and methyl alcohol. Methyl nitrite was volatilized at 50° to 60° C. in a water bath. Usatenko and Bulakhova (*317*) published directions for the dissolution of ore samples and removal of silica incident to the rapid determination of phosphorus.

A new reagent for the precipitation of sulfur was described by Belcher and Gibbons (*20*). Among the various complex organic compounds which were tested octoammino-μ-nitrodicobaltic nitrate gave the most complete precipitation of sulfate. Ethylenediaminetetraacetic acid was used to eliminate interference from aluminum and iron. Phosphate interfered if the pH was above 5. Precipitation was accomplished in the presence of acetone and was not as complete as that obtained by barium.

During the past decade the precipitation of barium sulfate has been the subject of several critical studies. The most recent published by Frey (*87*) recommended the elimination of foreign metal ions by the use of synthetic ion exchange resins. Coagulating reagents such as agar-agar were unnecessary and ignition temperatures should not exceed 600° C. Liang and Shen (*168*) found that tartaric or citric acid assisted in the purification of barium sulfate precipitated from a medium containing molybdic acid. Gandolfo (*97*) avoided the interference of iron in the recovery of barium sulfate by initial treatment with potassium iodide and subsequent removal of ferrous ferrite from a basic medium.

The disturbing effect of chromium(III) ion on barium sulfate precipitation was noted by Suzuki (*291*). Zinc amalgam was added to form chromium(II) and the reduced solution was added to a solution of barium chloride out of contact with air. Takagi (*293*) studied the effects of hydrochloric and nitric acids and their potassium salts on the precipitation of barium sulfate from solutions of ammonium sulfate. Hontoir (*130*) outlined the conditions which led to losses of sulfur in the preparation for the precipitation of barium sulfate during the analysis of iron pyrites. Among the factors which accentuated the loss were the use of iron mortars, crushing too rapidly, and overcrushing.

Two methods for the determination of sulfide sulfur in iron slags were examined by Ikegami and Morita (*134*). The standard evolution method was subject to error caused by the presence of acid insoluble sulfide. The preferred procedure was an indirect method in which the sulfide sulfur represented the difference between the total sulfur and sulfate sulfur. Methods involving this principle generally have restricted applications.

For those interested in the determination of sulfur in basic steel slags, Speight and his methods of analysis subcommittee (*284*) have recorded the results of a reconnaissance survey which indicated a serious lack of precision in sulfur determinations. After comparisons of four methods, two procedures were recommended; one of these, a barium sulfate precipitation, involved the dehydration of the dissolved sample with perchloric acid. The latter also removed fluorine more efficiently and dissolved any barium present as an impurity in the slag.

A modification of the Carius method for the determination of sulfur in both organic and inorganic compounds was discussed by Pristavka and Voticky (*229*). Oxidation required 20 to 40 minutes and deviations from the Carius method ranged from 0.04 to 0.39%. Mangan (*179*) used solvents for the selective extractions of various oxygen-sulfur groups. Lead salts were formed and a series of separations were made on the basis of the relative solubilities of these salts in water, ethyl alcohol, solutions of sodium hydroxide, and ammonium acetate.

Busch, Carter, and McKenna (*43*) and McKenna (*172*) tested critically the published methods for the determination of fluorine. With respect to gravimetric procedures they found precipitation as lead chlorofluoride superior to the calcium fluoride method. However, after a critical examination of the lead chlorofluoride method Saylor *et al.* (*261*) concluded that only within a narrow range of experimental conditions could a precipitate of theoretical composition be formed. The authors decided that the method would not give results reliable to better than 0.5%.

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Volumetric Analytical Methods For Organic Compounds

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THIS discussion endeavors to cover the literature from October 1951 to October 1953. A few earlier items which were not covered in previous reviews are also included. Although a large number of articles have appeared in this field, many of them are concerned primarily with modifications and adaptations of the more or less standard procedures. Some of these will be found to be useful improvements.

DETERMINATION OF ELEMENTS

CARBON

An improvement in the Van Slyke–Folch wet carbon combustion procedure increases the stability of reagents and convenience of handling by adding the chromic acid as potassium dichromate with the potassium iodate in the combustion tube instead of predissolved chromic oxide in the sulfuric-phosphoric acid solution (*163*).

A new apparatus for wet carbon combustion in which the sample is heated with the combustion reagent under reduced pressure is described (*162*). The carbon dioxide formed is diffused through a tube containing potassium iodide and zinc turnings into standard sodium hydroxide, the excess of which is titrated with hydrochloric acid after the addition of barium chloride.

HALOGENS

The results of about 100 experiments on the micro and semimicro-determination of halogens are tabulated to show the accuracy attainable by the following improved procedure (*84*):

> Samples of 10 to 20 mg. are burned at 1000° C. in a stream of 50 ml. of oxygen per minute. Chlorine is absorbed in a tube containing 2 ml. of $2N$ sodium hydroxide and 0.5 ml. of 30% hydrogen peroxide. The inlet tube and glass worm are washed with 1 ml. of 12% hypochlorous acid followed by 60 ml. of absolute ethyl alcohol. Five drops of 2,6-dinitrophenol and just enough $1N$ sodium hydroxide to give a yellow color are added, followed by 1 ml. of 0.4% mercuric chloride solution and 0.3 ml. of a 1.5% solution of diphenylcarbazide in absolute ethyl alcohol. The solution is then titrated with $0.1N$ silver nitrate in ethyl alcohol to a violet color.
>
> Bromine is absorbed in 5 ml. of $1N$ sodium hydroxide and the hydrogen peroxide is not added until after the combustion.
>
> Iodine is absorbed in 5 ml. of $1N$ sodium hydroxide without the addition of hydrogen peroxide. After the combustion and transfer, 10 drops of bromine are added, followed by 3 ml. of $9N$ sulfuric acid, formic acid, and sodium acetate. The final titration is made with sodium thiosulfate solution.

The usual inconveniences of some of the common methods for the determination of chlorine are reportedly avoided by placing the sample in a small porcelain crucible filled with halogen-free slaked calcium oxide and covering with a larger crucible and inverting. The small crucible is completely covered with calcium oxide and heated at a red heat for about 25 minutes until the mass is disintegrated. The contents are cooled, dissolved in 100 ml. of $2N$ nitric acid, filtered, and washed. The chloride is precipitated with silver nitrate and determined gravimetrically or volumetrically. The method is particularly convenient for polyvinyl chloride (*134*).

A modification of Votocek's method (*168*) for the determination of chlorine in organic compounds is based on the combustion of compounds wrapped in filter paper in a bottle containing distilled water in an oxygen atmosphere. The chloride is titrated mercurimetrically (*107*).

The reaction for the titration of fluoride with thorium nitrate is not the same as that between the fluosilicate ion and thorium nitrate. In the first case thorium tetrafluoride is formed, but hexafluothoric acid results for the most part in the latter reaction. Moreover, the second reaction varies, depending upon the way in which the fluosilicic acid is removed by distillation. The determination of fluorine when associated with organic material is accomplished by destroying the organic matter, removing the fluoride as fluosilicic acid by careful distillation from the ash mixed with 40 ml. of $18N$ sulfuric acid and 0.5 gram of silicon carbide, buffering a suitable aliquot of the distillate to pH 3.0, and titrating with thorium nitrate using sodium alizarin sulfonate as indicator (*170*).

In the determination of halo-organic compounds of the aliphatic series, the sample is placed in a rotating autoclave with $0.5N$ alcoholic potassium hydroxide and 10% aqueous sodium hydroxide for 1 hour at 200° (*131*).

METALS

The method of Schulek and Villecy (*140*) was modified for the determination of arsenic in organic nitrogen compounds of the guanidino type, by doubling the sulfuric acid, using less hydrogen peroxide, and adding the hydrazine sulfate in 10 ml. of water. Reproducible results were obtained with *N*-guanylarsanilic acid and its picrate (*156*).

A review (*13*) with 172 references discusses the determination of 38 metals in organic compounds.

NITROGEN

The Kjeldahl method is adapted to the analysis of azines, hydrazones, oximes, semicarbazones, other compounds containing N—O linkages, and derivatives of pyridine and quinoline. The material is dissolved in glacial acetic acid and methanol, reduced with zinc and hydrochloric acid, and digested, and the nitrogen is determined by Cole and Park's procedure (*47*).

A special apparatus for the Kjeldahl determination is described and analytical results for many substances are reported. The gas-volumetric Kjeldahl method is also described (*177*).

Nitrogen may be recovered quantitatively from a wide range of heterocyclic compounds and tetramethylammonium compounds by a Kjeldahl digestion using a mercury catalyst and a constant final ratio of sulfuric acid to sodium sulfate (*106*).

The method previously described for the determination of ring and side-chain nitrogen has been applied to other heterocyclic compounds. Acridine is not destroyed by ashing with sulfuric acid, but rings of pyrrole, indole, imidazole, pyrimidine, purine, thiazole, benzothiazine, and triazine are completely destroyed (*104*).

Preheating with thiosalicyclic acid assists the conversion of nitrogen to ammonia and permits the determination of nitrogen in nitro-type compounds in a method that appears to be suitable for all basic and neutral forms of nitrogen compounds found in petroleum (*97*).

The Ronchese and Colobraro modification of the Kjeldahl method was investigated on a semimicro scale by analyzing samples of urea, amino acids, and natural products (*25*).

Several investigations of factors influencing the Kjeldahl digestion have been reported.

In a study of the use of selenium oxychloride catalyst for the digestion of quinoline and quinaldine, it was observed that the time of heating and amount of catalyst were critical; an excess of either resulted in low results (*110*).

In a study of the effect of digestion temperature, it was found that a low temperature gives low results, while a high temperature results in loss of nitrogen. With the proper amount of potassium sulfate, the proper temperature of 410° C. may be obtained (*91*).

A modification of the Kjeldahl-Wilfarth-Gunning method reduces the digestion period to about 15 minutes by use of a higher concentration of mercury, intense heating, and silica granules. The method will stand less abuse than the method of the Association of Official Agricultural Chemists and requires more careful control of heating and measuring of chemicals (*119*).

Eight catalysts were used to determine nitrogen in samples of grasses, seeds, and leguminous plants. A mixture of selenium and mercuric oxide which gave maximum recoveries was selected as the best, although a mixture of selenium and mercury gave the shortest digestion period (*3*).

A special apparatus, together with a combination of existing methods, has been used for semimicro-Kjeldahl determinations (*145*).

A new method for the determination of nitrogen involves the combustion of the sample in the presence of powdered magnesium to form the nitride which decomposes in water to liberate ammonia, the latter being absorbed in a known volume of standard acid (*41*).

In a preliminary report on the Dumas method, Kirsten (*82*) reported that nitrogen can be determined accurately without mixing the sample with cupric oxide if a temperature of 1000° is used for the combustion. In a later report (*83*) nickel oxide was suggested as a better catalyst to replace cupric oxide, which gives incomplete combustion at low temperatures and liberates oxygen at higher temperatures to cause the retention of some oxides of nitrogen in the combustion tube.

Experimental results obtained by using an electrically heated apparatus in the micro-Dumas method indicated that in the reversible reaction $2CO_2 \leftrightarrows 2CO + O_2$ the equilibrium is completely to the left when carbon dioxide is passed at the rate of 10 bubbles per second through cupric oxide in a tube over a fixed heater at 450° to 600° C. When a movable heater reaches a temperature of 850°, the carbon dioxide rapidly dissociates to carbon monoxide and oxygen in the presence of cupric oxide and the nitrogen in the compounds is quantitatively reduced or oxidized to free nitrogen without the use of reducing copper, although copper is necessary for compounds containing halogen (*63*).

A titration procedure suitable for measuring the nitrate nitrogen content of nitrocellulose consists in dissolving the sample in hot acetic acid, boiling with a special ferrous salt reagent, and titrating the resulting ferric ion with standard titanous chloride solution using ammonium thiocyanate as the indicator (*142*).

OXYGEN

Several modifications of the Schütze-Unterzaucher method have been reported recently.

A careful study of the method has led to the development of an improved compact apparatus requiring little skill for routine operation (*23*).

The high blanks and extra corrections usually required can be eliminated by changing the volumetric iodine end point to a volumetric carbon dioxide one, and by improving the purity of the transport gas (*55*).

Difficulties due to the reaction of hydrogen formed by the pyrolysis and reduction of organic material with iodine pentoxide are avoided by the oxidation of the carbon monoxide to carbon dioxide by cupric oxide, and the collection of the carbon dioxide in a liquid nitrogen trap. After the residual gases are pumped out, the carbon dioxide is determined manometrically. Water is removed by freezing in a dry ice trap (*67*). An improved apparatus and procedure are described to overcome interference due to hydrogen, permitting accurate and rapid analysis of materials of both low and high oxygen content. The carbon monoxide formed is oxidized with iodine pentoxide, and the resulting carbon dioxide is absorbed in a measured excess of $0.05N$ alkali hydroxide solution, which is back-titrated with $0.025N$ acid after precipitation of the carbonate with barium chloride (*62*).

PHOSPHORUS

After destruction of the organic matter in glycerophosphates and lecithin with sulfuric and nitric acids, the phosphate is precipitated with a measured quantity of magnesium chloride hexahydrate in the presence of ammonium ion and ammonia. In the filtrate the excess of magnesium ion is titrated with $0.1N$ complexon III (apparently Versene, ethylenediaminetetraacetic acid) solution with a 0.4% solution of Eriochrome Black T in ethyl alcohol as indicator. The complexon III solution is standardized by titration of a solution containing 0.1 gram of zinc (*32*).

SULFUR

In a method for sulfur, the sample is oxidized with hot potassium dichromate in phosphoric acid. After the reduction of the excess dichromate by ethyl alcohol, the sulfate is precipitated with barium chloride. The barium sulfate which is contaminated with chromium is fused with sodium carbonate and potassium nitrate. The sulfate ion and other soluble material are extracted with hot water from the residual barium carbonate, which may be weighed, or dissolved in a measured volume of standard hydrochloric acid, and the excess acid then titrated (*85*).

Sulfur impurities from 0.1 to 0.001% in naphthalene, benzene, and phenol are determined by combustion of the sample in a hydrogen flame. The evolved gases are absorbed in hydrogen peroxide or sodium carbonate solution and titrated to a methyl orange end point. The analysis can be completed in 15 to 30 minutes. The accuracy decreases when larger amounts of sulfur are determined (*169*).

In a modification of the classical Carius method, potassium iodide is added to the sample, which is then moistened with water, treated with nitric acid, and fumed. Hydrochloric acid is added and the solution is boiled until colorless. The sulfur is then determined gravimetrically or by titration after precipitation with benzidine hydrochloride (*126*).

Sulfur can be determined by a procedure similar to the modification of Votocek's method for chlorine described above, by dissolving the combustion gases in aqueous hydrogen peroxide (*107*).

Sulfur is determined by combustion of the sample in the presence of magnesium to form magnesium sulfide by a process similar to that described above for nitrogen. When dissolved in acid, the hydrogen sulfide which forms is absorbed in a suitable train (*42*).

TELLURIUM

The sample is completely decomposed by heating with nitric acid. After the addition of more nitric acid and phosphoric acid the sample is diluted and an excess of $0.1N$ potassium dichromate is added. After 30 minutes, an excess of standard ferrous solution is added and back-titrated with standard dichromate using diphenylaminesulfonate as indicator (*90*).

FUNCTIONAL GROUPS

ACIDS

A method for the determination of formic acid has been described (*100*) wherein the mercurous salt, formed by reaction of mercuric acetate or chloride with the acid, is titrated with an iodide-iodate solution.

The free and total acidity in commercial lactic acid (*45*) was estimated by titration followed by hydrolysis with excess standard alkali on another sample. It was found in the determination of lactic acid in heavy corn steep liquor (*151*) that oxidation procedures employing potassium permanganate were more satisfactory.

ACID ANHYDRIDES

Application of the Mahn-Nodeau procedure (*148*) for acetic anhydride to propionic, maleic, phthalic, camphoric, and butyric anhydrides was successful. Succinic anhydride gave anomalous results.

Acid anhydrides, in the presence of organic acids, have been determined (*66*) by reaction with excess methanolic morpholine, followed by titration of the excess with methanolic hydrochloric acid to a dimethyl yellow–methylene blue end point.

An improved procedure for the determination of acetic anhydride by reaction with aniline, followed by a diazometric titration, is described by Parravano (*118*).

ACTIVE HYDROGEN

The procedures for the determination of reactive hydrogen have been reviewed (*117*) for possible application in the estimation of reactive structural units in coal degradation products.

It has been found that lithium amides of dibutylamine, butylamine, piperidine, and pyrrolidine (*60*) can be successfully employed for the determination of active hydrogen in alcohols and phenols.

ALCOHOLS

Improvements in the acetylation procedure of Verley and Bolsing (*165*) for the determination of primary alcohols are described (*121*).

The higher aliphatic alcohols can be determined more rapidly than by acetylation methods if a procedure is employed involving esterification of the alcohol with excess lauric acid in the presence of a *p*-toluenesulfonic acid catalyst (*120*).

Ethyl alcohol, in the presence of various solvents such as benzene, ether, acetone, acetaldehyde, ethyl acetate, or camphor, can be estimated quantitatively (*112*) by conversion to the volatile ethyl nitrite, which is removed from the solvent by a stream of carbon dioxide, and followed by conversion to nitrous acid, which is determined iodometrically.

The optimum conditions for the quantitative oxidation of ethyl alcohol to acetic acid have been determined (*43*). It was found that the oxidation depended more upon the temperature than upon the time of reaction, the optimum temperature being 70°. The concentration of sulfuric acid in the chromate mixture was an important factor in the oxidation.

An acidimetric procedure for the determination of glycols using sodium periodate (*31*) is described. A sample of the glycol is permitted to react with excess sodium periodate and the excess is titrated with dilute sodium hydroxide using a thymolphthalein-naphthalbenzein indicator. A blank is determined by the titration of an equal volume of periodate solution to the same color end point.

The use of an isopropyl acetate solvent in the place of ether has been suggested for the periodic acid oxidation of glycerol (*74*).

Small quantities of glycerol can be estimated (*101*) by oxidation with excess permanganate followed by back-titration with oxalic acid.

Druce has given directions for the determination of glycerol present in trace amounts in sugars (*36*).

ALDEHYDES AND KETONES

The most widely used method for the determination of aldehydes and ketones is the oximation procedure of Bryant and Smith (*19*) or some modification thereof. The procedure has been tested by independent workers (*109*) on 140 carbonyl-containing compounds.

Modifications in the hydroxylamine procedure have been worked out with special reference to the determination of carbonyl compounds in fatty acid oxidation products (*44*) and for the determination of ketones (*114*). Alcohols, esters, hydrocarbons, and acids do not interfere in the ketone determination.

Free organic acids, however, do interfere in the determination of heliotropin by the hydroxylamine method (*133*). The error may be eliminated by the use of a dimethyl yellow–methylene blue indicator in the place of bromophenol blue.

Aldehydes, in mixtures obtained from combustion products of hydrocarbons (*8*), can be determined by passing the solvent through a column packed with silver oxide and titrating the effluent with potassium thiocyanate. A correction factor is necessary to obtain accurate results.

A procedure for the determination of formaldehyde and aromatic aldehydes is described by Siggia and Segal (*149*). The sample is allowed to react with an excess of laurylamine and the excess amine is titrated potentiometrically with salicyclic acid.

Several procedures are available for the estimation of formaldehyde. The majority of these involve reaction with excess potassium cyanide, the procedures differing mainly in the method employed for the determination of the excess cyanide. Bring (*16*) and de Jong (*75*) both recommend the use of mercuric salts for the determination of the excess cyanide. Other workers (*88*) have converted the excess cyanide to cyanogen bromide with excess bromine, the excess being removed by the addition of phenol, and the cyanogen bromide is determined iodometrically.

The bisulfite method is said to be successful in the determination of formaldehyde in the presence of its polymers (*71*).

Application of the bisulfite method to the determination of acetone gives only fair results (*72*).

Since the determination of furfural by a volumetric bromide-bromate method gives results 2% high, precipitation procedures are recommended (*17*).

A modification of the method of Schöniger and Lieb (*136*) has been used in the determination of methylglyoxal (*124*).

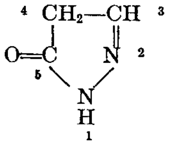
The sample is added to a 20-fold excess of a hot 20% solution of *m*-nitrobenzohydrazide in 10% acetic acid. After heating, the precipitate is filtered, washed with 10% acetic acid, then with water, and is finally dissolved by boiling for 5 minutes in a known volume of titanous chloride to which 60 ml. of a 37% hydrochloric acid solution has been added. The excess titanous chloride is titrated with ferric alum to a thiocyanate end point.

AMINES

The application of nonaqueous solvents to the determination of weak bases has been extensive. The solvent generally employed is glacial acetic acid and the titrating agent perchloric acid. Applications of this acid pair to weak base determinations have been reviewed (*7*).

Purine bases (*34*), secondary and tertiary fatty amines, and amino nitriles (*161*) have been estimated by titration with perchloric acid in glacial acetic acid. A crystal violet indicator was employed in these determinations.

Pyrazolones (I) (*166*) can be titrated in glacial acetic acid with perchloric acid if a pyrazole structure can be realized by shifting of *H* from C_4 to N_2 (II) or to the carbonyl oxygen (III).



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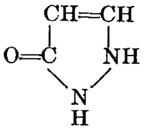

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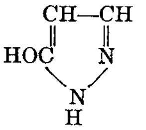

III

Amines have also been determined in nonaqueous solvents using differential titration procedures (*50*). The method permits the analysis of aromatic-aliphatic amine mixtures as well as other mixtures of the following types: aniline-*o*-chloraniline, pyridine-caffeine, and aniline-sulfathiazole.

Nonaqueous solvents have also been employed in the determination of amine salts (*48*). The salt is dissolved in an ethylenediamine or dimethylformamide solvent and titrated with sodium methoxide in a methanol-benzene mixture using a thymol blue or an azo violet indicator.

Ammonium reineckate has been suggested as a reagent for the determination of organic bases (*116*). The sample is dissolved in 0.1*N* hydrochloric acid and an equal volume of water and is then precipitated with a 0.5% ammonium reineckate solution. After 2 to 24 hours, the precipitate is filtered, washed, and decomposed by heating with Fehling's alkaline Rochelle salt. After the addition of 25% nitric acid and an excess of silver nitrate, the excess silver ion is determined with ammonium thiocyanate.

Aromatic amines may be determined by titration with a sodium nitrite solution. The end point has been detected by the use of starch-iodide paper (*56*) or by application of the dead-stop end-point technique (*137*).

Special methods have been applied in the determination of individual compounds. Melamine is determined by precipitation as the semioxalate and titration of the oxalic acid in the precipitate with potassium permanganate (*154*) while quinoline is estimated by utilization of the following reaction (*87*):

$$C_9H_7N + K_2Hg(SCN)_4 \rightarrow C_9H_7N.Hg(SCN)_2 + 2KSCN$$

The crystalline complex is removed by filtration, the excess reagent is converted to potassium thiocyanate and mercuric oxide, and the thiocyanate is determined argentometrically.

PEROXIDES

A method, employing stannous chloride as reductant, has been developed for the analysis of organic peroxides (*9*).

> The sample containing the peroxide is dissolved in acetic acid under a nitrogen atmosphere. A known volume of standard stannous chloride solution is added, and the reaction vessel is evacuated and filled with nitrogen. After 1 hour, a boiling stock ferric solution, ammonium chloride, and water are added. The mixture is kept at 70° for 30 seconds, and cooled rapidly, and phosphoric acid solution is added. The ferrous iron is titrated with potassium dichromate solution. A blank is run in a similar manner.

Small amounts of organic peroxides have been determined iodometrically employing the dead-stop end point technique (*1*).

PHENOLS

Phenols and substituted phenols may be titrated in nonaqueous solvents. Most phenols with negative substituents are sufficiently acidic to permit the titration in dimethylformamide with an azo violet indicator (*51*). Phenols and alkyl phenols can be titrated in ethylenediamine with sodium methoxide using an *o*-nitroaniline indicator.

The potentiometric titration of weak acids in ethylenediamine with sodium aminoethoxide developed by Moss, Elliott, and Hall (*111*) has been modified and adapted to the determination of phenols in coal oil (*79*).

Since phenol acetates hydrolyze rapidly during hydrolysis of an acid anhydride, which usually occurs at the end of the acetylation reaction, a modified procedure is described (*18*). The acetylating reagent is prepared by mixing acetic anhydride with ten times its volume of pyridine. The sample is heated for 2 hours under a reflux condenser on a water bath. The acid formed is titrated with 0.5*N* potassium hydroxide to the phenolphthalein end point. The determination of phenols by the *p*-nitrosodimethylaniline method is discussed (*115*).

Resacetophenone has been determined to within 5% by titration with bromide-bromate, plotting the initial bromate against excess bromate (determined iodometrically) and extrapolating to zero excess to give the bromate equivalent to dibromination (*113*).

SULFIDES AND DISULFIDES

A modification of the procedure of Siggia and Edsberg (*147*) has been employed in the determination of aryl and heterocyclic sulfides (*68*). The sulfide is oxidized with excess bromide-bromate solution and the excess determined iodometrically. Any sulfide can be determined by the bromide-bromate oxidation if the dead-stop end-point technique is employed.

Disulfides, in the presence of thiols, have been determined by removal of the thiols through reaction with acrylonitrile, followed by reduction with zinc and subsequent titration of the resulting thiol with silver nitrate (*37*).

SULFOXIDES

The following procedure has been recommended for the determination of sulfoxides (*10*).

> The sample containing approximately 1 meq. of sulfoxide is dissolved in 10 ml. of acetic acid. The reaction vessel is evacuated and filled with nitrogen, 15 ml. of a 0.1*N* titanous chloride solution is added, and the flask is re-evacuated and refilled with nitrogen. After being immersed in a water bath at 80° for 1 hour, a boiling solution (5 ml.) of ferric alum, diluted with 50 ml. of water, is added. The solution is rapidly cooled, 10 ml. of a phosphoric acid solution is added, followed by 15 ml. of carbon tetrachloride, and the ferrous iron is titrated with 0.05*N* dichromate solution using a diphenylaminesulfonic acid indicator (6 drops). Allylic sulfoxides are reported to give low results.

THIOLS

Thiols in hydrocarbon gases have been determined by oxidation with a cupric acetate reagent containing excess acetic acid (*38*). After the oxidation, potassium iodide is added. Part of the iodine liberated by the excess cupric ion oxidizes mercaptide to the disulfide. The remaining iodine, which is equivalent to the residual cupric ion after the thiols are completely oxidized, is titrated with sodium thiosulfate solution. The difference between the original and residual cupric ion represents the equivalents of thiol in the gas sample.

UNSATURATION

A new method has been described for the estimation of unsaturation using a constant stream of ozone as the titrant and employing a suitable dye as the indicator (*14*). The ozone is prepared by the electrolysis of dilute sulfuric acid by a generator which maintains a constant stream of ozone if the current input is constant. The method is accurate to 1 to 2% in all compounds tested with the exception of diisobutylene, where the results were consistently 6% high.

Acetylenes and monosubstituted acetylenes have been determined in the presence of butadiene (*69*) and in the presence of other four-carbon hydrocarbon fractions (*128*) by precipitation of the acetylenes with silver nitrate in ethyl alcohol followed by titration of the liberated nitric acid.

The method has been applied with success to some ethynyl carbinols (*70*) using a slight modification. The excess silver ion is determined in the precipitating agent or it is determined in the solution resulting from the action of nitric acid on the precipitated acetylide.

The reaction of disubstituted acetylides with mercuric acetate in water to liberate 2 moles of acetic acid has been used to estimate disubstituted acetylenes. The liberated acetic acid is titrated with standard alkali (*89*).

MISCELLANEOUS METHODS

MIXTURES

A determination of 1,2-propylene glycol in ethylene glycol is based on oxidation of the 1,2-propylene glycol to iodoform and subsequent determination of the iodoform by treatment with an excess of standard silver nitrate, followed by titration of the excess silver ion by the Volhard method (*76*).

Mixtures of aliphatic volatile aldehydes, ketones, and combined carbonyl compounds can be determined by suitable application of the hydroxylamine hydrochloride method, in which the hydrogen chloride liberated on oxime formation is titrated with standard alkali (*21*). By "combined carbonyl compounds" is meant acetals and cyclic aldehyde polymers. Total aldehydes and ketones are determined at room temperature and pH 5 to 6. Aldehydes are destroyed by silver oxide oxidation to the nonvolatile salt of the acid (a safety shield is recommended) and the ketones and combined carbonyls are then steam-distilled into hydroxylamine hydrochloride at pH 5 to 6. Under these conditions only the ketones react. Total carbonyl is found by reaction at pH 1 to 3 and elevated temperatures. The minimum error often exceeds 2% in practice.

By suitable combinations (*11*) of methods previously described for the independent determinations of hydroperoxides and sulfoxides (*6, 7*) mixtures of the two substances may be satisfactorily analyzed for each component. It is necessary to divide a given sample into two aliquots, one of which is analyzed for peroxide, the other for total peroxide plus sulfoxide.

Mixtures of glucose and ascorbic acid may be analyzed by determining the ascorbic acid iodometrically and determining ascorbic acid plus glucose with Fehling's solution. Results are not exact (*8*).

A mixture of ethyl alcohol and ethyl ether may be analyzed for both components by passing the gaseous mixture first through Cordebard's reagent (potassium dichromate in nitric acid) (*28*) which oxidizes the alcohol to acetic acid, and then through nitrosulfochromic acid to oxidize the ether. The amount of each oxidizing agent used is calculated by determination of the excess remaining after the oxidation (*40*).

Mixtures of alcohol, ether, and water have been analyzed by use of a calibration graph constructed from data obtained by determining the boiling point and by adding dibutyl phthalate reagent and titrating with water to a permanent opalescence (*65*).

In analyzing a mixture of maleic and phthalic acids, the total acidity may be determined by titration with alkali, and the maleic acid may be determined by oxidation with acidic permanganate, followed by determination of the excess permanganate by the addition of potassium iodide and titration with thiosulfate (*73*).

SILICON DERIVATIVES

The Karl Fischer reagent can be used for the titration of most silanols and silanediols, according to the following equation:

$$R_3SiOH + I_2 + SO_2 + 2CH_3OH \longrightarrow R_3SiOCH_3 + 2HI + CH_3HSO_4$$

Some compounds, such as tri-1-naphthylsilanol and tri-*o*-tolylsilanol, do not react to an appreciable extent (*53*).

SUGAR AND DERIVATIVES

The determination of aldoses by oxidation with iodine in alkaline solution has been discussed (*157*).

Somogyi has described a copper reagent for use in connection with the iodometric technique for sugar determination (*152*).

Sodium borohydride has been used in the following way for the determination of reducing carbohydrates. A sample of the sugar is treated first with a standard sodium borohydride solution adjusted to pH 9 to 10. The excess of borohydride is decomposed by addition of sulfuric acid to bring the pH to about 1. The hydrogen liberated is collected and measured in a gas buret (*93*).

Sen and Ghosal (*141*) report that in the estimation of reducing sugars with potassium ferrocyanide, the sharpest end point is obtained when a 0.3% solution of alkaline potassium ferrocyanide is titrated with the solution of reducing sugar in the presence of a 1% solution of methylene blue as indicator.

The Luff-Schoorl reductometric method (*138*) is reported to give false results in the presence of amino acids. Dipeptides show less influence and polypeptides or albumin have no appreciable effect (*160*).

Whistler, Hough, and Hylin (*171*) have shown that D-glucose in corn syrup can be determined by use of glucose dehydrogenase. In the presence of oxygen the enzyme oxidizes D-glucose to D-gluconolactone, which is determined quantitatively with standard alkali.

Under some conditions the presence of ferric salts, ammonium salts, magnesium sulfate, and magnesium chloride may cause incorrect results in the iodometric determination of reducing sugars (*150*).

WATER

Mitchell (*108*) has discussed the Karl Fischer reagent and its applications, and has given detailed directions for the determination of water in carbonyl compounds, xanthates, dithiocarbonates, penicillin, organic hydrates, and dehydrated foods.

The end point in the Karl Fischer determination is made more easily discernible by the addition of a few drops of a solution of methylene blue in absolute alcohol or pyridine. The reagent solution becomes green at first, then dark green just before the end point, and finally dark green in reflected light and Bordeaux red in transmitted light (*46*).

UNCLASSIFIED

The following reaction is used as the basis for an interesting procedure for determining theophylline and theobromine (*86*).

$$2\ \text{theopyhlline}\,.\,\text{Na} + K_2Hg(SCN)_4 \rightarrow (\text{theophylline})_2Hg + 2KSCN + 2NaSCN$$

A 0.2-gram sample is placed in a 100-ml. volumetric flask with 3 to 4 ml. of water, 1 drop of phenolphthalein, and sufficient carbonate-free alkali to give a pink color. An excess (30 ml.) of $0.05N$ $K_2Hg(SCN)_4$ is added dropwise. If necessary, a few drops of $0.1N$ sodium hydroxide are added to maintain the pink color. The solution is boiled cautiously for 20 minutes, cooled, diluted to 100 ml., and filtered. To 50 ml. of the filtrate is added 30 ml. of $0.05N$ silver nitrate solution, and after acidification with 10% nitric acid the excess silver nitrate is titrated with $0.05N$ potassium thiocyanate solution in the presence of ferrous ammonium sulfate indicator.

Wolff and Bister (*174*) have described an iodometric procedure for the determination of caffeine, which avoids the disadvantage of older procedures where the approximate caffeine content must be known before the sample is analyzed.

By the substitution of magnesium oxide for sodium sulfite as an iodine trap in the procedure of Rupp and Lemke (*130*) the method may be used for determining both iodine and mercury simultaneously (*30*). The silver iodide formed is removed by filtration and weighed, and the filtrate is titrated with thiocyanate to give its combined silver and mercury content. Since the original amount of silver added is known, the mercury content can be calculated.

A method for determining the methylol content of phenol alcohols and one-stage phenolic resins is based on the action of a phenol with a phenol alcohol to form a bis(hydroxyphenyl)-methane and water (*103*). The reaction is catalyzed by *p*-toluenesulfonic acid and the water formed is collected in a calibrated take-off trap and measured. With pure phenol and benzyl alcohols the results are always within 3% of the calculated values.

Schulek and Boyer (*139*) suggest the following three methods for determining allyl alcohol: (1) direct titration with bromate in the presence of acid and an alkali bromide, using a suitable indicator such as *p*-ethoxychrysoidine; (2) addition of an excess of bromate with subsequent iodometric back-titration; and (3) titration of the acid produced on reaction with bromine water. In this last method one equivalent of acid is produced per mole of allyl alcohol. It is suggested that the bromine addition product hydrolyzes readily to give 1-bromopropanediol.

An iodometric determination of propargyl alcohol is based on the following reaction (*175*):

$$HC{\equiv}CCH_2OH + I_2 + OH^- \rightarrow IC{\equiv}CCH_2OH + I^- + 2H_2O$$

A sample of 20 to 60 mg. of the alcohol is diluted to 10 ml. with water and 25 ml. of 1*N* sodium hydroxide solution and 25 ml. of 0.1*N* iodine solution are added. After 10 minutes, 35 ml. of 0.1*N* sulfuric acid is added and the excess iodine is titrated with 0.1*N* sodium thiosulfate.

At higher concentrations or at elevated temperatures some $I_2C = CICH_2OH$ is formed and the equation given above does not hold. If formaldehyde is present in the sample, it will be oxidized by the iodine. Correction for this can be made by determining the formaldehyde separately by the hydroxylamine method.

Various methods for determining simple ethers (*125, 143, 146, 167*) have been compared (*144*) for their applicability to vinyl propyl and vinyl isopropyl ethers. Hydrolytic oximation in the presence of hydroxylamine hydrochloride gave satisfactory results as long as the mixture contained no more than 20% ethyl alcohol. Hydroxylamine sulfate does not give complete oximation. The iodometric method in an ethyl alcohol solution gave good results with mixtures regardless of the amount of alcohol present.

2,3-Dihydropyran can be determined by bromination in a benzene-water mixture, using 100% excess of potassium bromate–potassium bromide and hydrochloric acid with mercuric chloride as a catalyst. The excess bromine is determined iodometrically (*96*).

The method of Biedermann and Schwarzenbach (*14*) for titrating alkaline-earth ions with ethylenediaminetetraacetic acid can be reversed so that the latter compound can be determined by titration with magnesium chloride or magnesium nitrate solutions (*80*).

Jouslin has described a method for the analysis of alkylaryl sulfonates in which the sample is converted by alkaline fusion to the corresponding phenol, which is then determined by a bromination procedure (*77*).

In another method, the sulfonate is converted to the acid by the treatment with hydrochloric acid, and by suitable titrations both the total acidity and the acidity due to hydrochloric acid may be determined (*39*).

A method suitable for the routine analysis of anion-active, colloidal electrolytes used as detergents depends on complex formation with *p*-toluidine hydrochloride. The complex is extracted with an organic solvent and titrated with standard alkali. In calculating results, use must be made of an empirically determined factor which depends on the molecular weight and the number of solvatable groups (*159*).

Sodium oleate in concentrations of 10^{-3} to $10^{-4}M$ can be determined by titration of a mixture of aqueous cetyl trimethyl ammonium bromide and chloroform with sodium oleate solutions at pH 10. Near the end point, methylene blue is added as an indicator and the titration is continued until the intensity of the color is the same in both the aqueous and organic phases (*54*).

A technique described as a solubilization titration appears to provide a rapid method for the analysis of binary mixtures of organic liquids. The method depends on the observation of one or both of the two best-marked phase changes that occur when a relatively polar organic compound, such as an alcohol with five or more carbons, is added to a mixture of a less polar organic liquid, such as a hydrocarbon, and a soluble amphiphilic salt solution. When 5 ml. of hexane with 5 ml. of Teepol is titrated with 1-octanol the following phase changes occur: (1) progressive solubilization of the organic liquids in the aqueous phase, finally giving a clear, isotropic solution; (2) progressive precipitation of a liquid crystal phase; (3), progressive resolution of the precipitate formed in the second phase; and (4) progressive precipitation of the aqueous phase from the solution. A graph prepared from known mixtures may be used in the analysis of an unknown mixture (*95*).

A modification (*4*) of previously described methods (*98, 99*) for the estimation of thiourea is described as avoiding the erratic results of the earlier procedures.

Rhodanides, isothiocarbamides, thiocarbamates, thiols, xanthogenates, thiosemicarbazones, and methylthiouracil have been determined in the following way.

> The sample is dissolved in alcohol, 1*N* sodium hydroxide solution, or water and, if necessary, the solution is made ammoniacal. The solution is titrated with 0.1*N* silver nitrate solution. The precipitate is removed by filtration; the filtrate is acidified with concentrated nitric acid and then back-titrated with 0.1*N* ammonium thiocyanate solution (*105*).

Lasco and Peri (*92*) have used a somewhat similar method for determining 1-naphthylthiourea (ANTU).

A determination of dithiocarbamates is based on acid decomposition of the sample and subsequent determination of the carbon disulfide formed. The evolved carbon disulfide is washed with lead acetate solution to remove hydrogen sulfide and sulfur dioxide arising from sulfide and thiosulfate impurities, and is then absorbed in potassium hydroxide solution and titrated with standard iodine solution (*24*).

Wojahn (*173*) reports that thiosemicarbazide and its derivatives can be titrated with sodium hypoiodite solution.

The allethrin content of commercial allethrin samples is determined by reaction with ethylenediamine to form an equivalent quantity of the amine salt of chrysanthemum monocarboxylic acid, which is then titrated with standard sodium methylate in pyridine. If any chrysanthemum monocarboxylic acid, anhydride, or acid chloride is present, it must be determined independently and suitable corrections made (*66*).

Benzene solutions of triphenylmethyl react quantitatively with excess benzoyl peroxide. By determining excess peroxide iodometrically with potassium iodide and acetic acid, the determination of hexaphenylethane may be accomplished (*57*). In this reaction, the products formed may vary with the concentration of the reactants, but the peroxide consumption will be unaffected.

A rapid iodometric determination of nitrogen, nitro, nitroso, isonitroso derivatives, and diazo compounds is based on the fact that hydrogen iodide, acting as a reducing agent under certain temperature conditions, liberates an equivalent of iodine which is characteristic for every nitrogen function. The sample is heated at 100° to 300° in a sealed glass tube in a metal container along with hydriodic acid, and the iodine formed is determined by titration with standard thiosulfate solution. A complete run must be made on the hydriodic acid alone to obtain a blank correction (*2*).

A new analytical method, based on the microdiffusion principle of Conway (*26*), has been proposed for the determination of trimethylamine oxide in fish. The trimethylamine resulting from reduction with titanium chloride is neutralized by acid and the excess of the latter is titrated (*64*).

Trimethylamine in choline salts has been determined by passing air through a solution of the choline salt in sodium hydroxide and then through acetic acid to absorb any volatile amine. The amine is then titrated with perchloric acid in acetic acid. The air is passed through the salt solution for 75 minutes at a temperature of 25° to 30°. At 40° the choline decomposes into volatile amine (*29*).

Bucci (*20*) has described a procedure for the determination of thioglycolic acid in the presence of sulfite, thiosulfate, and sulfide, whereby the sulfite and part of the thiosulfate are precipitated in neutral solution as barium salts by the addition of excess saturated barium nitrate solution, and the remaining thiosulfate and sulfide and thioglycolic acid are precipitated in the filtrate by the addition of 2.5% silver nitrate solution. The thioglycolic acid is liberated by the addition of $9N$ hydrochloric acid and is then titrated with $0.1N$ iodine solution.

Acid or alkaline hydrolysis of the weed killer, 3-(*p*-chlorophenyl)-1,1-dimethylurea, can be made to produce quantitative yields of *p*-chloroaniline, dimethylamine, and carbon dioxide, and can thus serve as a basis for determination of the urea (*94*). After acid hydrolysis (with $0.2N$ sulfuric acid), the dimethylamine is determined by back-titration of the hydrolysis mixture with $0.15N$ sodium hydroxide solution. The end point must be determined by electrometric methods to prevent interference by the chloroamine. When basic hydrolysis is used, the dimethylamine is distilled into standard acid and the excess is back-titrated.

Urea and urethan have been decomposed by sulfuric acid hydrolysis and the resulting ammonia is liberated by alkaline steam distillation and determined by collecting in standard acid (*129*).

Barbituric acid derivatives can be titrated in a mixture of purified pyridine bases, either potentiometrically or with thymol blue or phenolphthalein indicators (*59*).

The determination of anthracene based on the reaction of anthracene with maleic anhydride (*123*) has been applied to the determination of small amounts of anthracene in tar oils and tar-oil fractions (*135*).

In the titration of sodium glycerophosphate, the use of methyl orange–xylene cyanole as an indicator is recommended (*172*). Advantages are the sharper end point and the coincidence of the faint violet end point with the true potentiometric equivalence point.

1,1,2-Trichloroethene in air is absorbed on silica gel, then taken up by an air current at 140°, saturated with water, and passed through a quartz tube at 900° to 1000° to form hydrogen chloride which may be either titrated or determined gravimetrically (*33*).

Crotonaldehyde has been determined in the following way (*164*).

> To 5 ml. of aqueous solution are added 10 ml. of $0.01N$ iodine solution and 1 ml. of $1N$ sodium hydroxide. After 45 minutes, 2 ml. of $1N$ hydrochloric acid is added and the liberated iodine is titrated with $0.01N$ thiosulfate. A blank is necessary.

It appears that oxidation reagents such as $KCu(IO_4)_4$ containing trivalent copper or $KNi(IO_4)_5$ containing quadrivalent nickel may be useful in the determination of compounds containing hydroxyl or amino groups on adjacent carbons (*12*).

By using ceric sulfate as an oxidizing agent and titrating the excess with ferrous sulfate, a great number of organic compounds may be determined (*81*). Among the compounds for which this method is useful are mono- and polyhydric alcohols, mono-, di-, and trihydric phenols, aminophenols, aromatic amines, and materials of high molecular weight such as starch, agar, and carboxymethylcellulose.

p-Aminosalicyclic acid dissolved in hydrochloric acid is diiodinated so rapidly by iodine monochloride that the reaction has been made the basis of a quantitative determination (*52*).

Liquid zinc amalgam has again been used in analytical chemistry. In a recent application cystine is reduced in $2N$ sulfuric acid under carbon dioxide in 2 to 3 minutes. The amalgam is then removed and the solution is titrated at 3° to 9° C. with potassium iodate (*176*).

In the estimation of indigo and indigo carmine, sodium vanadate has been recommended as superior to permanganate as the oxidizing agent. The excess vanadate may be titrated with a ferrous sulfate solution (*127*).

Small amounts of phenolphthalein have been determined by an iodometric procedure (*153*).

The determination of hexobarbital and sodium hexobarbital by the manganobromometric method has been modified by replacing potassium bromate with potassium permanganate (*78*).

A study has been made (*61*) of the possible use of indicators for the titration end point in the volumetric determination of various functional groups which react with lithium aluminum hydride.

The reduction of nitroguanidine proceeds rapidly at room temperature with the consumption of 6 equivalents of trivalent titanium when carried out with at least a 200% excess of titanous chloride in a weakly acidic citrate buffered solution (*155*). The excess titanous chloride is titrated with a standard ferric alum solution. Results for nitroammonocarbonic acids average almost 3% low.

Titrations in nonaqueous media receive continued study and application. The application of the Brønsted theory to titrations in glacial acetic acid has been described, and results are reported for the titration of alkaloids, alkaloid salts, salts of organic acids, pyrazolone derivatives, and sulfonamides (*5*).

The addition of an excess of a solvent with a low dielectric constant is reported to give a marked increase in the sensitivity of the end point in both visual and potentiometric titrations of weak acids, bases, and salts (*122*).

Choline salts of carboxylic acids have been determined by titration with $0.1N$ perchloric acid in acetic acid, using crystal violet as the indicator (*102*).

Fritz (*49*) has discussed the scope and limitation of the titration of imides and enols as acids in nonaqueous media. The titration is carried out with standard sodium methoxide. Suitable indicators, depending on the acidic strength of the compound to be titrated, are thymol blue, azo violet, and *o*-nitroaniline.

The recent interest in the drug isonicotinic hydrazide is reflected in the number of procedures which have been reported for its determination. Titration with $0.1M$ sodium nitrite solution (at ice bath temperatures) leads to the formation of the azide, and is reported to be rapid and accurate (*22*). Another method is based on the reaction of the hydrazide with ammoniacal silver nitrate to give silver, nitrogen, and isonicotinic acid (*132*). The excess silver nitrate is titrated with standard thiocyanate solution. Other methods are based on the reaction of the hydrazide with iodate. Direct titration with $0.5M$ potassium iodate may be used (with *p*-ethoxychrysoidine as indicator) (*35*), or the iodine liberated may be titrated with thiosulfate (*158*). Bromometric procedures have also been described (*27, 58*).

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Biochemical Analysis

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DURING the past 2 years, progress in biochemical analysis has been most apparent in the extension of techniques to new applications, and in refinements and modifications to increase the utility or applicability of methods, rather than in the invention of new basic methods. Zone electrophoresis is notable in the rate at which it has developed and expanded in application. Especially significant is the fact that it has been accepted as an almost routine procedure for clinical study as well as for its more obvious research applications.

Tremendous interest continues in the various phases of chromatography, and it is these two preparative approaches that are outstanding in the biochemical analysis field. In the more strictly quantitative aspects of the field, there has been an increased use of enzymes as analytical reagents. For years, enzymes have served largely to increase the specificity of methods—e.g., uricase to destroy uric acid—so that the interfering reducing agents could be determined separately. Analysis by means of enzyme systems is an expected development and will have to be reckoned with as a factor of significance in future developments. It is considered premature to attempt its detailed review here. A more quantitative approach to cellular chemistry through microphotometric technique and fractional isolation of fixed cell structures is also apparent. Some other techniques previously reviewed (*259*) have shown increased utilization. A general view of the field fails to note many new trends in biochemical analysis. Certain newer techniques of the analytical chemist such as amperometry, coulometry, and high frequency titrations have not yet been adopted widely for biological systems, though their use has increased. In general, instrumental methods have remained of secondary importance except for those common instruments long used by the biochemist and the chromatographic and electrophoretic instruments and techniques.

PREPARATIVE METHODS

In keeping with the distinction (*259*) between procedures that serve to isolate, fractionate, or prepare for analysis, and those that serve to determine the amount of the material after this preliminary preparation, the subjects discussed here are divided into preparative and determinative procedures.

CHROMATOGRAPHY

It is questionable if any technique of the biochemical analyst has exerted so profound an effect on the field so rapidly as has chromatography. The mass of literature describing the applications of this technique is now so great as to preclude here any exhaustive review. It has been covered up to 1952 in several monographs (*19, 37, 105*). Trends are now apparent that could not be so clearly delineated in earlier reviews. Ion exchange has continued to be an important aspect of chromatography, with some new applications, and wider general use. The development of low-cross-linked resins makes possible the adaptation of ion exchange techniques in fields previously closed to it. The use of ion exchange in preliminary deionization of solutions prior to partition chromatography (*52, 394, 424*) and for preliminary group fractionations (*45, 61, 346*) is notable. Emphasis is diminishing on some phases of column chromatography other than ion exchange, as compared with the greatly increased application of paper partition methods. It appears that with proper choice of conditions, almost any mixture can be separated on paper and, by extension to include cellulose columns, the identification technique can be scaled up into a preparative technique. The general field of chromatography has been reviewed by Tiselius (*489*) and Moore and Stein (*347*).

PAPER CHROMATOGRAPHY

While the application of paper chromatography is now almost universal, the problems of detecting the fractions and particularly of determining them quantitatively remain difficult ones. A wide variety of new or modified methods for these purposes have been developed. Labeling the materials with radioactive isotopes and measuring the activity of the spots or zones by radioautography or the Geiger-Müller counter have been extended as a general technique (*194, 331, 419*), applied to studies of photosynthesis (*23*), applied to radioactive sugars by Putman and Hassid (*398*), and applied to organic phosphate esters by Cohen and Oosterbaan (*96*). An interesting application to amino acid analysis by means of their complexes with copper-64 was developed by Blackburn and Robson (*35*), who applied the technique to the complete analysis of salmin sulfate. The rather obvious but neglected technique of scanning paper chromatograms with a high frequency apparatus was described by Hashimoto and Mori (*202*). Scanning methods with visible and ultraviolet light have been widely used (*59, 408, 433*). A number of absorptiometric scanning devices and techniques have been described (*74, 266, 320, 353, 485*) with inclusion of ultraviolet absorption (*49, 135, 190, 203, 304, 379*), which has been applied to nucleic acid derivatives (*135, 304*), ketosteroids (*485*), and plant phenols (*49*). An interesting variation of the scanning technique was described by Sulser and Högl (*479*), who photographed the chromatogram and used the reduced reproduction for scanning.

Basic studies for improving the ninhydrin determination of amino acids have been reported (*60, 215, 462, 506*) as well as substitute methods for detecting amino acids (*255*). Some investigators have restudied the application of the micro-Kjeldahl method for this purpose (*260*). Fluorescence has been adapted to the detection and determination of some constituents for which it is favorable (*447*) such as vitamin C (*368*), while, in at least one instance, microdiffusion technique was employed for quantitative determination of amines (*445*).

The mechanism of paper chromatography (*66, 229*) and particularly the factors that influence the R_f value (*81, 148, 157, 269, 529*) have been rather carefully investigated. Previously buffered papers have been adopted by several investigators (*296, 319, 320*). Interest in reducing the scale and increasing the precision of separation of components on paper is reflected in a number of publications describing techniques of smaller than conventional scale (*14, 407*), in which the highest possible resolving power and greatest sensitivity are sought.

At least one ultramicromethod utilizing thoroughly washed thread for ascending chromatography has been described (*496*). This type of development cannot fail to extend the utility of the method, as will also the interesting and rapid technique of circular paper, or horizontal chromatography. This was first developed by cutting a strip inward from the edge to the center of a circular filter paper, dropping the tab so formed into the solvent reservoir, and allowing the materials separated to form complete rings from a central initial spot at the anchor of the tab (*428*). The spreading of a spot into a relatively large ring so reduced the concentration per unit area that the technique did not find great use, in spite of the horizontal migration which was highly reproducible and which eliminated the effect of gravity on the speed of solvent advance. The employment of a central wick surrounded by a number of samples placed as spots in a circle proved far more advantageous because the fan-shaped chromatogram developed by each spot avoided excessive dilution and led to narrow bands instead of spots in the developed chromatogram. It also allowed direct comparison of different samples on the same paper. This technique has been developed most extensively by Giri and coworkers (*167, 176, 404*) but has also been used in this, or a modified form, by various others (*310, 402, 405, 435*) and may have developed more or less independently in several laboratories. It has also been developed into two-dimensional operation (*175*).

A promising technique is based on the salting-out principle of Hagdahl and Tiselius (*193*), who increased the adsorption of dyes, proteins, peptides, and amino acids on paper by raising the salt content and eluted fractions by lowering the salt content by steps. Similar technique was described about simultaneously by Taira *et al.* (*481*). Countercurrent partition on paper (*124*) was achieved by using one ascending solvent and a descending solvent simultaneously, so arranged as to meet just above the sample.

An important limitation of paper chromatography was the difficulty of separating proteins in unchanged condition. That this has been at least partially overcome is indicated by the reported successful paper chromatography of proteins (*114, 152, 382, 484, 530*) and especially of enzymes (*71, 171, 248, 409, 453*), though many applications to enzyme study have been through the chromatographic identification of the products of enzyme action (*123, 174, 196, 272, 322, 492*). Paper chromatography, which generally uses organic solvents, cannot be expected to produce results in the separation of proteins that will compare with the much more favorable technique of paper electrophoresis.

As has been true almost from the inception of paper chromatography, major interest still continues in amino acid and polypeptide separation, identification, and determination from the standpoint of method (*40, 169, 170, 172, 173, 177, 213, 296, 369, 391, 401, 403, 429, 512*) and for numerous specific purposes, including analysis of proteins (*168, 281*), resolution of the optical isomers of tyrosine and glutamic acid (*432*), determination of peptide end groups (*235*) and terminal amino acids of bovine plasma albumin (*136*), of ovomucoid (*389*), and of hypophysial growth hormone (*300*), clinical studies of amino acid metabolism (*313, 330*), and comparative studies of the blood amino acids of mammals (*129*), insects (*15*), and silkworms (*158*). The specific problems of chromatography of protein split products as it applies to amino acid metabolism were reviewed by Awapara (*17*), and a more general comparative review of this technique in comparison with other types of fractionation procedures was published by Boulanger and Biserte (*45*). Extension of the important application to nucleic acid derivatives has also continued with development of valuable improvements (*77, 264, 327, 422, 449, 483*).

An increased interest in carbohydrate isolation and identification by paper chromatography is evident (*27, 34, 120, 137, 220, 323, 337, 346, 355, 364, 400, 416, 426, 477*). More significant is the fact that the earlier techniques, most of which required the formation of the 2,4-dinitrophenylhydrazones, have been largely replaced by direct chromatography of the uncombined sugar. Great proportionate increase in experimental activity attaches to the steroid hormones and related fat-soluble materials such as vitamin A and E, phospholipides (*291*), and fatty acids (*236*) which were difficultly chromatographed by early techniques. Some investigators have reversed the phase or altered the paper characteristics by treating the paper with hydrophobic or other special materials such as silicone (*59, 275*), paraffin (*138, 236*), triglycerides (*467*), Quilon (*273*), acetylating agents (*336*), propylene glycol (*436*), and formamide (*527*). Paper has also been coated with alumina for this purpose (*452*), though its behavior is then more closely akin to column than to paper chromatography. Proper choice of solvents for fat-soluble materials has made possible more conventional paper separations (*18, 207, 212, 247, 265, 343, 431, 443*) and the 2,4-dinitrophenylhydrazones have been utilized (*533*). Applications of these methods to clinical studies of steroid hormones have been described (*117, 324,* *329*) and the subject has been reviewed (*13, 211*). A useful and rapid qualitative technique for lipide mixtures as they occur in tissues was described by Hack (*192*).

Organic acids, when present in mixtures such as biological materials, have not been simple to identify or to determine individually by chemical methods. Paper chromatography has brought welcome relief to this problem. It has been employed for study of volatile fatty acids (*249, 302*), but more often for di- and tricarboxylic acids (*61, 92, 113, 166, 214, 249, 376, 511*). Studies of identification procedures after chromatographic separation are available (*3, 65, 303*). Keto acids in blood and other physiological fluids have been extensively isolated on paper in the form of 2,4-dinitrophenyl-hydrazones (*84, 85, 206, 278, 446*). An interesting variation was the reduction of the keto acid hydrazones to amino acids, which could then be separated and identified chromatographically (*277*). The method has also been successful in separating isomers of keto acids (*475*). Column methods for organic acid separation have also been popular.

The intimate role of phosphates in metabolism of carbohydrates, in muscle contraction, absorption, photosynthesis, and many other physiological processes, as well as the occurrence of phosphates in nucleic acid derivatives and other physiologically significant compounds, has led to continued application of paper chromatography to the study of phosphate esters (*20, 67, 96, 123, 131, 149, 427, 500*) with specific application to the myokinase system (*139*) and to the study of photosynthesis (*23, 63, 351*). A reversed phase technique for certain phosphate esters was described (*334*). Paper chromatography has been applied to a wide variety of special types of compounds. These include vitamin B_{12} (*387*), urinary pantothenic acid (*107*), nicotinic acid derivatives (*6*), oxidation forms of coenzyme A (*233*), flavonol aglycons (*119*), flavones (*82, 375, 383*), rutin (*374*), bile acids (*274*), porphyrins (*140, 448*), imidazoles (*9*), monosubstituted guanidine derivatives (*418*), indoleacetic acid determination (*524*), hydroxyphenylalkylamines of barley germs (*142*), choline esters (*508*), sympathomimetic amines (*509*), circulins and polymixins (*126*), and peptide components of lichens (*499*). An interesting application was made to the chromatographic patterns of tissues for various plant and animal species (*69*), which were found to be very individual. A number of recent reviews of paper chromatography are available (*141, 237, 525*) and the application of the technique to food analysis (*468*), to microbiology (*397*), and to taxonomic studies of various species (*70*) has been discussed.

ION EXCHANGE

The specific uses of ion exchange resins during the past 2 years have not developed the large bibliography characteristic of the field of paper chromatography. Two possible reasons for the smaller bibliography are: The separation of individual organic ions does not require novel conditions, solvents, or test reagents. Ion exchange resins provide rational means of pH adjustment without added electrolyte, and of deionization or fractionation, so that the use of resins may pass unmentioned in the title or abstract of a paper.

While specific citations are unnecessary, certain "modern" resins are characterized by resistance to attrition and degradation, existing as graded beads of a variety of sizes. They possess unifunctional groups and are supplied with various degrees of cross linkage throughout their plastic matrix. From the research point of view, it is important that the functional groups conferring the charge character be of a single chemical type. Thus, ambiguous ion exchange behavior may result from the use of a resin which contains monoalkyl ammonium charges, if the resin is of the phenol-formaldehyde type. At one pH value, the resin may behave as an anion exchanger (expected); at a higher pH value, the resin may behave as a cation exchanger (unexpected).

The past 2 years have seen the rise of the polystyrene resins to a unique position in the ion exchange field. As these resins are styrene-divinylbenzene copolymers, various degrees of three-dimensional rigidity and stability are possible, being controlled by the content of divinyl benzene in the polymer matrix. The research man has the opportunity to test five or more quaternary ammonium polystyrene resins as anion exchangers at the present time. Presumably these resins *have identical capacities and* charged groups, differing only in the amount of crosslinking. The Dow Chemical Co. has been especially progressive in making available these varieties of resins, and has followed the helpful policy of complete chemical description of both the functional groups and the plastic matrix of their resins (*93*). The structure of the polystyrene sulfonate resin (Dowex 50) stems from the work of Bauman and Eichorn (*25*). The structure of the quaternary ammonium polystyrenes (Dowex 1 and 2) is described by Wheaton and Bauman (*507*). The physical-chemical aspects of the behavior of these and other ion exchange resins are reviewed by Boyd (*46*), Bauman *et al.* (*24*), and Juda *et al.* (*251*).

Ion exchange resins are used to remove undesired ions from sugar or phosphate ester mixtures before paper chromatography (*131, 518*), from gelatin (*246*), from enzyme solutions during dialysis (resin on nonprotein side of dialysis membrane) (*165*), or from spinal fluid proteins (*133*) prior to paper electrophoresis. In such applications the resins are serving as "molecular sieves" (*386*). The choices of particular resins and their use in serial columns or single "monobed" column are dictated by the ability of the compound of interest to withstand the acidic environment around the sulfonic acid groups of the cation exchange resin and/or the high alkalinity in the vicinity of resin beads holding $—N^+(CH_3)_3OH^-$ groups. This follows from the requirement that the resins should be in their acidic and strongly basic forms for true deionization to occur. Woolf (*518*) indicated that deionization of sugar solutions was not possible using Amberlite IR 400 in its free hydroxide ion form, but was possible using the resin in its bicarbonate form. Here deionization is essentially complete, since the carbonic acid formed may be easily removed. Another alternative treatment of the sugar solution involved the use of a mixed bed of a sulfonic acid resin and a weakly basic resin. The later resin prevented exposure of the sugar to local regions of high pH. The efficient removal and fractionation of individual organic anions and cations by exchange resins are useful and often serve to concentrate individual ions prior to isolation. The generality of this review precludes mention of the numerous individual applications of the ion exchange technique. The carboxylic acids which occur in plant extracts or tissue extracts are capable of separation using anionic resins (*62, 68, 377*). Busch *et al.* (*68*) were able to separate common acids of the citric acid cycle from silica gel or Dowex 1 resin, using gradient elution. The elution technique provides for gradually increasing acid eluent, giving the fractionation a certain automatic character and providing for sharpened boundaries for every fraction (*489*). Various correlative reviews are available concerned with individual applications of ion exchange and the use of the technique in analysis (*26, 36, 118, 179, 279, 356, 434, 491*).

The full power of the ion exchange technique has been demonstrated in the fundamental work of Cohn's group at Oak Ridge. Their careful fractionation of hydrolyzates of ribose nucleic acid has resulted in the separation and identification of four pairs of isomeric nucleotides. The quaternary amine resins, Dowex 1 and 2, have been used; Amberlite IR 400 may also be used for some of the fractionations, if desired. As an example of Cohn's work, one pair of isomeric nucleotides is believed to comprise adenosine-2 -phosphate and adenosine-3′-phosphate (*57, 83, 308*). With care in selection of elution agents, these compounds as well as adenosine-5′-phosphate, adenosine-5′-pyrophosphate, and adenosine triphosphate can all be separated in one ion exchange analysis, using milligram and even gram quantities of starting mixture. Paper chromatography will also achieve the separation of most members of this series, but ordinarily on the microgram scale (*77, 80, 463*). The ultimate development in the separation of nucleotides is represented by a system and apparatus capable of automatic monitoring of fractions coming from a column and of electronic decision concerning the particular collection vessel to receive the fractions (*115*, *116*).

Similarly, the development of a careful elution scheme by Moore and Stein (*216*, *349*, *472*) has resulted in the separation of the 17 common amino acids from each other. The amino acids are placed upon the sulfonated polystyrene resin (Dowex 50) in the form of their cations ($HOOC.CHR—NH_3^+ Cl^-$). Elution of specific amino acids is obtained by incremental changes of pH, ionic strength, and temperature. The separation method allows determination of the amino acid composition of pure proteins on a few milligrams of sample, with possibility of standardization of procedure among laboratories on a world-wide scale. A further improvement has led to the proportional upscaling of the process as a preparatory method for various amino acids (*216*). An additional refinement is the use of volatile ammonia-ammonium formate buffers, as the particular amino acid may be freed of solvent (water) and eluent electrolyte in one operation. In order fully to appreciate the triumph described above, it is necessary to scan a review of pre-ion exchange times, such as the 50 pages devoted to this subject in 1938 (*72*).

While space precludes detailed attention to the work of Cohn's group or that of Moore and Stein and their coworkers, several general aspects may be observed. As stated in the previous review (*261*), the emphasis of recent biochemical analysis "has been upon carefully devised fractionation schemes coupled with rapid and reasonably accurate determinations using family properties and reactions." Such a statement is even more appropriate at this time than in 1952. Thus, Cohn's fractionation schemes are dependent upon routine measurement of light absorption at 260 mμ, and upon absorption ratios determined by measurements at the first wave length and at 280 mμ. Similarly, the work of Moore and Stein has used the "family" reaction of all amino acids with ninhydrin (*348*) to yield a dependable, determinable colored product.

A scheme for the separation of purines, pyrimidines, certain vitamins, and the various amino acids (*503*, *504*) depends upon the examination of the fractions for ultraviolet absorption, and for visible absorption after the amino acid-ninhydrin reaction is carried out in the usual way. Partridge (*384*), drawing upon long experience in the ion exchange separation of amino acids by displacement development (*385*, *386*), has proposed a scheme for the separation of water-soluble extractives, leading first to separation into bases, acids, and neutral compounds. A second procedure fractionates the bases by displacement development of the cation exchange column which holds them as a group. A similar process is applied to the grouped acids on the anion exchange column. No single scheme is yet available for strict quantitative analysis even for all nitrogenous constituents. It will be necessary to perfect hydrolysis methods of more universal application and to obtain more accurate information regarding the fractionation of naturally occurring ampoteric substances in relation to the ion exchanger and to the pH.

Moore and Stein have used various techniques which may find application in other ways in addition to amino acid fractionation and analysis. Among these may be mentioned the use of a nonionic detergent to speed equilibria in the successive sections of the resin column, and the use of benzyl alcohol as a component in the buffers used to strip aromatic amino acids from the resin bed. One could wish that the nonionic detergent possessed a short descriptive name, other than BRIJ 35 (*349*).

As these authors point out (*347*), "the successful separation of organic compounds attained on ion exchange cannot be ascribed solely to differences in the ionic nature of the solutes. . . . Thus glycine, alanine, valine, and leucine, amino acids of identical charge, are fully separated on Dowex 50 by virtue of the greater affinity of the resin for the longer aliphatic side chains."

Ion exchange resins will perform many functions for the biochemist, regardless of their complete chemical composition. However, for projects of the type undertaken by the groups associated with Cohn and with Moore and Stein, it would seem essential that resins of reproducible and known characteristics be used, so that such work will not require repetition as better resins appear. There may be secondary effects in the fractionation processes developed by both groups which will be found related to the common polystyrene matrix of the resins they now use. Correlations regarding such common effects would be impossible if one group had used phenol-formaldehyde resins and the other polystyrene resins.

The application of ion exchange to aldehydes and ketones (*159*, *228*, *456*) and to hexoses (*456*) as bisulfite derivatives has extended the use of resins to compounds previously immune to fractionation by this method. At its present stage, the method of Samuelson *et al.* (*159*, *456*, *457*) does not allow fractionation of homologous ketones with the finesse of the previously outlined schemes. One difficulty seems to reside in the choice of eluents: water or alcohol-water mixtures. The ketones appear as such in the effluent. Taking a cue from the work of Khym *et al.* (*258*, *528*), with dissociable borate-sugar anionic complexes, it would seem profitable to elute the carbonyl compounds with bisulfite or bisulfite-sulfite buffers, so as to maintain the charged derivatives during complete passage through the resin column. Sulfur dioxide removal thereafter should present no problem. Indeed, using the process outlined in these publications, it is likely that such resin columns are loaded with sulfur dioxide bubbles, unless the pH is maintained constant in the eluent mixture employed.

The work of Khym, Zill, and others of the Oak Ridge group has broadened application of ion exchange to include fractionation of certain pentoses, hexoses, and disaccharides (*258*, *528*) from a mixture. The eluting agent is sodium tetraborate or a buffer including trace concentrations of borate. The complex is thus maintained at a high level at all times, and little free sugar exists until a later borate-removal step of the scheme. The technique was first applied to glycerol purification (*526*), and has been used for the separation of ribosides (*240*) and sugar phosphates (*257*). Noggle and Zill (*363*, *364*) have applied the method to separation of six common sugars of plant extract origin.

Attempts to devise a rational separation scheme for peptides (*127*) on Dowex 50 have emphasized the necessity for fully characterized resins. These authors found that broad elution curves were obtained using the commercial 8 to 10% cross-linked resin. On samples of 4% crosslinkage, sharp elution curves were obtained. The more open styrene sulfonate resin allowed the desired equilibria for the separation of leucylglycine and glycylleucine from each other and from other dipeptides. Again, reversible adsorption is in part responsible for the discrimination obtained.

The necessity for resins of "correct" cross linkage is also illustrated by the isolation procedure used for coenzyme A (*469*). Coenzyme A possesses a molecular weight of approximately 770; it exchanges on Dowex 1 as a phosphate ester anion. The purification step is necessary for the removal of contaminating adenosine phosphates which lack the coenzyme activity. These nucleotide contaminants elute more readily from the column and may be discarded. The coenzyme A fraction is later eluted. In this work it was necessary to use a 2% cross-linked resin, such resins being very closely related to soluble polyelectrolytes, as Juda, Marinsky, and Rosenberg (*251*) point out. Such resins must have a less rigid three-dimensional structure than is possessed by resins containing 8 or 10% divinylbenzene. Accessibility of the coenzyme A to the total number of charged groups on these highly solvated resins is assured, even when the coenzyme A "dimerizes" by the A—SH to A—S—S—A oxidation.

Ion exchange resins may serve several purposes in protein chemistry, provided rather rigid criteria are obeyed. Using a highly cross-linked resin of large bead size, one may remove small, rapidly diffusible ions (*133*, *246*, *386*, *410*, *411*), the proteins passing through the resin column without appreciable adsorption loss.

If a resin of fine mesh or low degree of cross linking is used, chromatographic fractionation of proteins may occur. Separations of egg white proteins (*465*) and standard mixtures (*464*) on fine-mesh, highly cross-linked Dowex 50 have been reported. Uniquely defined fractionations of cytochrome (*325, 358, 381*), ribonuclease (*217, 218*), and lysozyme (*482*) have been obtained using a fine-mesh form of the carboxylic resin, IRC 50. The separation of hemoglobins on this resin was successful only in part (*39*).

Carboxylic resins of lower degree of cross linking may provide routine chromatography of the basic proteins. Such resins, with their high affinity for hydrogen ions, are not likely to provide separation of the more acidic proteins, where the protein can exchange as a cation only at pH 5.0 or lower. If chromatography of a protein occurs, one still must estimate the extent of "denaturation" occurring in the process, before success is implied. Moore and Stein (*347*) have cautioned: "Optimism arising from the results with IRC 50 should be tempered by the realization that successful chromatography. . . has only been achieved with markedly atypical, unusually stable basic proteins. . ."

In addition to precise fractionation of homologous acids and bases, ion exchange resins continue to provide routine determinations of total cation of serum (*396*) or of "pure" specimens of organic salts after crystallization (*495*). Resins may also be employed to prepare standard alkali in situ for use in immediate titrations (*189, 473*). It is especially useful for generation of $0.001N$ alkali (*189*), as this dilute titrant is quickly neutralized by atmospheric carbon dioxide, if exposed. However, such titrants undoubtedly contain traces of alkyl amines from hydrolysis of functional groups of the resin, so a continuously flowing effluent is probably the most dependable standard titrant (*189*).

Indirect fractionation of an extremely weak acid from a strong acid has been demonstrated by staff members of the Dow Chemical Co. (*125*). The process has been patented and has been termed ion exclusion. It results from the process called Donnan distribution, as applied long ago to protein gel interactions with electrolyte. Bauman and Wheaton (*26*), in an extension of the same type of investigation, have determined that such diverse hydroxyl-substituted compounds as sucrose, glycerol, triethylene glycol and phenol may be separated reasonably well from one another. This separation is provided by reversible adsorption, since none of these are ionized, except at very high pH values.

Time and space do not permit review of the field of catalysis by ion exchange resins, except to mention that members of Cohn's group have used Dowex 50 to catalyze the hydrolysis of adenine nucleotide, forming adenine cation which remains on the resin, and ribose phosphate which passes into the effluent. Any adenosine formed by hydrolysis of the ribose phosphate linkage is also held on the resin, while inorganic phosphate then appears in the effluent.

The field of ion exchange resins in membrane form is in robust infancy. Results obtained with Permionic and other resin membranes were discussed in the reviews of Bauman *et al.* (*24*) and Bergsma (*31*) and recent developments have been reported (*252*). A biochemical application to the determination of calcium ion binding by bovine albumin has been reported in detail (*79*).

ADSORPTION AND COLUMN PARTITION CHROMATOGRAPHY

Adsorbents of Natural Origin. While ion exchange resins possess the ability to fractionate the majority of "biological" compounds, there are limitations to the use of resins in certain cases. These limitations may be summarized as follows: (*a*) the inability to fractionate compounds of nonionic character—e.g., fats, sterols, carbohydrates, etc.; (*b*) technical difficulties in the use of solvents during elution; (*c*) lack of resin of a desired function and cross linkage—e.g., the carboxylic self-buffering resin is not yet available in varieties of cross linkage.

The limitations stated as (*a*) and (*b*) usually occur simultaneously, since one desires to use solvents to increase the solubility of most nonpolar compounds, and to fractionate while using those solvents. Under such conditions, there may be appreciable solubility of a resin so that fractions are contaminated, and the remaining resin in the column is changed in behavior. No rational fractionation of nonelectrolytes on ion exchange resins has been reported, except for the work on ion exclusion (*125*) and its extension to hydroxyl-substituted compounds (*26*).

Partition chromatography, where an inorganic or organic gel immobilizes the aqueous phase, is closely related to paper chromatography and shares certain characteristics with countercurrent distribution. Developments in either of the two latter fields should provide advances in the column partition technique. On a theoretical basis, van Duin (*130*) suggests that once the true retention volumes are known for a homologous series, one may be able to identify an unknown from interpolation of the value for the unknown upon the logarithmic graph for the series.

Organic acids may be separated by partition on alumina (*12*), on Celite (*393*), on silica gel (*64, 494, 519, 520*), and on silica gel using gradient elution (*328*). In a series of investigations of steroid transformations in the perfused bovine adrenal gland, a group working with Jeanloz and Pincus (*297*) has followed the conversion of deoxycorticosterone to corticosterone, using activated carbon for adsorption of plasma steroids, and silica gel columns for the fractionation of corticosteroids. Ketosteroids have also been fractionated on silica gel containing nitromethane (*250*), or on alumina (*534*). The steroid alcohols may be esterified with benzoic acid and chromatographed on alumina (*56*). Pregnandiol (*109*) may be separated from various urinary contaminants and purified, using alumina. The vitamin A alcohol and its ester have been separated from fish oils on alumina (*156, 493*), enabling a more accurate determination by the usual colorimetric methods.

Attempts to apply column chromatography in one plane have led to the use of a glass strip covered with silica gel for the separation of dinitrophenylhydrazones (*371*). In this use, the advantage of silica gel over paper chromatography is not apparent. Borke and Kirch (*43*) have coated glass strips with a complex mixture including silicic acid, calcium sulfate, and magnesium oxide, together with a phosphor mixture. They developed a chromatogram on this surface, for various opium analogs, and were able to locate each area of interest by the quenching of fluorescence under ultraviolet illumination.

Partition chromatography on starch has provided an amino acid analysis of an ACTH protein preparation from sheep pituitary (*333*), and the use of starch has been proposed, surprisingly, for the quantitative determination of pentoses and aldohexoses (*162*). In the latter case, the reducing contaminants from the starch were minimized by the use of alcohol water mixtures, lacking acid, for the elution. Methods employing cellulose as adsorbent have been developed for keto acids (*128*), for raffinose in raw sugar solutions (*188*), and for indole derivatives from plant extracts (*146*). Continuing efforts toward exploitation of reversed-phase partition chromatography are represented by the separation of bile acids on silane-treated Celite (*32*) and the isolation of estriol from pregnancy urine by partition chromatography using a gel of rubber particles (*44*).

The pioneer work of Tiselius, Claesson, and others (*489*) has utilized activated carbon and known mixtures of homologous alcohols and acids. This combination has been used for minute investigation of the process involved. Here, one is concerned with adsorption-elution or adsorption-displacement, rather than with partition chromatography. Work of this type is proceeding in Tiselius' laboratory (*7, 8, 489, 515*) and has been continued by Holman (*195*), using the simplified interferometer monitor of Holman and Hagdahl (*224*). The series of reports by Holman and coworkers (cf. *195*) has involved the separation of saturated fatty acids and of important unsaturated aliphatic acids, and the displacement analysis of steroids.

Tiselius (*489*) considers that the chromatographic separations which utilize adsorption followed by displacement by a compound of high adsorption affinity may consist of this process alone, in which case compound A and compound B may overlap in concentration in the fractions, or an additional factor may be exploited. The additional variable may be the deliberate inclusion of a series of alcohols in the column run in which amino acids are being fractionated, for example. The alcohols will arrange themselves according to affinity between amino acids, so that the desired compounds are not cross-contaminated with each other. This process is termed "carrier displacement chromatography" (cf. *489*). Differing from this process only in degree is the "amplified chromatographic separation" reported (*282*).

An improved elution technique, from practical standpoints, is that of gradient elution (*7, 8, 68, 515*). Here, the elution agent exists in a concentrated form, but is applied to a column with a linear rise of concentration through the successive fractions appearing in the collector. It is accomplished by interposing a reservoir of solvent between the column and the stock solution of eluting agent. The reservoir is continually mixed by magnetic stirring or other sealed stirrer, while the stock solution enters the reservoir at a rate identical with the delivery of diluted stock solution to the column. Thus, a gradient of eluting agent develops in the column, and each eluted compound is found in a more sharply defined fraction than in the ordinary technique. Presumably, such an elution technique is not restricted to any single type of column, and gradient displacement may also be possible. An interesting comparison may be drawn from the work of Busch *et al.* (*68*), since gradient elution of members of the citric acid cycle was possible with both silica gel and Dowex 1 (formate) resin as adsorbents.

The purification of peptides and proteins has been investigated in several ways, using ion exchange on the carboxylic resin (*218, 358*), kieselguhr after silane treatment (cf. review *347*), starch (*147*), paper chromatography (*453, 484*), paper electrophoresis (*330, 460*), and the special adsorbents discussed below.

The gonadotropic proteins from pregnancy urine have been adsorbed on kaolin, eluted, and chromatographed on calcium phosphate gel (*108*). ACTH peptide mixtures have been purified with active carbon and carrier displacement technique (*301*), but more general use of oxycellulose columns has been made (*28, 53, 164, 414*). Richter *et al.* (*414*) were able to use buffered IRC 50 resin to effect some purification of their ACTH preparation. The resins of low cross linkage should replace oxycellulose as an adsorbent for peptides, especially when a carboxylic resin becomes available in this form. The caution voiced by Moore and Stein concerning chromatography of proteins (see Ion Exchange) should be considered.

Paper (*289*) and cotton fabric (*191*) have been treated so as to enhance their ion exchange character by introducing carboxyl groups, sulfonic acid groups, etc. This work is handicapped by a lack of knowledge of the amorphous portion of the cellulosic chains which will accept the substituents and exhibit the ion exchange behavior later. Such materials may serve as substitutes for exchange columns or ion exchange membranes, but surely will not serve thereafter in the ordinary paper chromatography.

Recent attempts have been made to design adsorbents specifically for a particular use (*73*). Thus, Lerman (*293*) has treated cellulose with diazotized *p*(*p*-aminobenzene)azobenzene arsonic acid to yield an adsorbent which specifically binds antibody protein. Thereafter sodium arsanilate adjusted to pH 8 was employed as eluting agent, applied by the gradient elution technique. The isosteric sulfanilate could not replace the arsanilate as the elution agent. A similar attempt has been made by Brown and Watson (*58*) to design an adsorbent for fractionation of the presumably macromolecular desoxyribonucleic acid. Here histone protein was "immobilized on the surface of kieselguhr" by a method to be described in another article. The column of histone-kieselguhr served to separate a preparation of desoxyribonucleic acid into seven fractions, on elution with increasing sodium chloride concentrations. The fractions of desoxyribonucleic acid were definitely of differing composition, as measured by their content of purine and pyrimidine bases. Further developments will be watched with interest.

Gas-Liquid Chromatography. James and Martin (*244*) have developed a chromatographic separation for volatile acids, nitrogen being mobile and a kieselguhr-silicone mixture being the stationary phase. The method is capable of a great degree of automaticity, as the acids arrive at the collection point free of accidental acids, and repetitive titrations with alkali may be done in a simple manner. In a series of successive papers, the authors have applied similar chromatography to analysis for amines (*245*), higher aliphatic amines and pyridines (*242*), and constituents of volatile minerals (*243*). The last paper serves to summarize the authors' work in detail. The method fills a need for rapid determinations of the short-chain fatty acid composition of mixed glycerides such as ordinary neutral fat.

ZONE ELECTROPHORESIS

Electrophoresis on paper or other porous support has shown very rapid development and application in the past 2 years. The technique is so simple, as compared with its alternatives, as to offer a very attractive research and routine method. Paper electrophoresis rests fundamentally on the same basic theory as the earlier Tiselius free boundary method, and is therefore readily interpreted compared to the more empirical chromatographic methods. It avoids one of the serious limitations of the earlier techniques, control of convection, but introduces certain other variables such as paper participation in the electrophoretic movement, and additional interfaces that may be troublesome under some circumstances. Complications from the investigation of electromigration in a capillary system make strict interpretation difficult, but this does not interfere in any way with comparative results which are usually the ones sought.

The chief disturbing factors in the actual electrophoresis are (*a*) evaporation; (*b*) denaturation (of proteins); (*c*) electroendosmosis; and (*d*) movement of solvent through failure to level the end vessels. Additional factors during continued use are (*e*) changes in the buffer composition through electrolysis products, and (*f*) convection in the end vessels, ultimately allowing back-electrophoresis of electrolytic products.

Factors (*a*) and (*b*) are related primarily to the current density, since the heat generated is equal to I^2R/cm.^{2}. The rate of movement of any ion depends on the voltage drop per unit distance. Though some investigators have recommended high voltages (*225, 261, 337*), it would appear that moderate ones would provide differential separation of undenatured protein, since heat generation is increasing proportional to I^2. Elaborate cooling devices have been recommended by some investigators (*150*) and simpler ones are widely used. Many workers achieve essentially the same results at low voltage gradients with no cooling. Immersion in a coolant liquid was popular at one time, but has been largely abandoned. Evaporation is also a function of the type of vessel surrounding the paper strip. Sandwiching the paper between glass plates has been most common, but many investigators now suspend it on glass rods (*101, 271, 315, 362, 501*) or hang it free in the air in an enclosed vessel (*284*).

Factor (*c*) is impossible to avoid when paper is used as support material. In precise work it may be measured and applied as a correction, using a neutral substance whose movement is readily detected (*259, 342*). As none of the movement comes from electromigration, the electroendosmosis is measured. Electrolytic alteration of the buffer is unavoidable. Convection and back-electrophoresis of the products are avoided largely by proper design of the end vessels. Designs range from simple liquid containers with no precautions against these effects to the other limit of elaborate multicompartment cells (*315*). The matter is clearly of secondary importance except in continuous operation for long periods, because it is largely subject to control by frequent renewal of the solutions in the end vessels.

The paper itself, which serves as an "inert" support which minimizes convection, has been replaced by silk (*163*), powders, glass beads, starch and gels (*488*), and starch alone (*280*). Aqueous systems have been replaced by nonaqueous in the effort to separate fat-soluble materials (*389*). Electrophoresis has been combined with chromatography on the same paper as a second operation (*262, 385*). It has also been modified as a batch preparative method for proteins (*201*), by using very thick paper, and as a continuous preparative method (*184*). Two-dimensional electrophoresis has been described (*474*), as has an interesting technique termed electrorheophoresis, in which the solvent is allowed to evaporate continuously at controlled temperature (*312*). The electrophoretic movement in one direction, opposed by the physical movement of buffer up the strip in the other direction, is stated to lead to very sharp lines for each protein constituent separated. The capacity of the apparatus has been greatly increased by using several paper layers sandwiched between thick cellophane strips (*366*). Numerous designs of apparatus have been described recently (*161, 180, 186, 284, 315*), most of which represent minor modifications of earlier designs. Extensive studies of the relationship of variables such as pH, ionic strength, time, and voltage to the rate of migration have been made (*317, 318, 466, 517*) and comparative studies with classical electrophoresis are available (*21, 143, 326, 466*).

Paper electrophoresis, as well as the "ancestral" free boundary method, has proved especially suitable for protein separation and determination. As Kunkel and Tiselius (*281*) have pointed out, zonal electrophoresis is an advance over free boundary methods, in that simultaneous separation of multiprotein mixtures is obtained. All types of electrophoretic separation have outdistanced competitive methods in view of the mild conditions and reagents employed. This last statement is true only if acid or alkali gradients do not develop and all electrode products are efficiently removed. Direct use with serum proteins (*161, 186, 283, 295, 399*) and especially clinical applications (*11, 33, 51, 156, 183, 187, 197, 254, 263, 309*) have been numerous. Applications to animals other than man, and particularly to comparative studies of blood proteins of different species, have shown some very significant differences in the species patterns (*10, 99, 437*) and in that of mammals *vs.* nonmammals (*178*). General studies of protein separation by paper electrophoresis, and of proteins from sources other than blood, are extensive (*225, 234, 354, 497, 522, 523*). Thus, cerebrospinal fluid (*338, 392, 395*), urine (*460*), and muscle proteins (*326*) have been subjected to this type of study. Particular interest has attached to the investigation of lipides bound to proteins (*145, 361*), carbohydrates bound to proteins (*100, 267*), and binding of such materials as blood iodine (*230*), dyes (*253*), and iron (*231*).

As with paper chromatography, the detection of the bands or spots on the paper has required much research in the case of proteins, and numerous procedures have been advocated. Direct staining with a variety of dyes, sometimes followed by photometric evaluation, has been most widely employed, and some novel techniques have been suggested (*48, 143, 283, 373, 420, 505*). Special scanning devices have been described for this purpose by several investigators (*286, 287, 372*). Scanning is made more exact when hydrophobic material of proper refractive index such as a mixture of liquid petrolatum and α-bromonaphthalene (n = 1.51) (*263*) or methyl salicylate (*285*) is applied to make the paper transparent. The protein-dye combination is often eluted for quantitative photometric determination (*161, 180, 186, 234*) or for Kjeldahl determination (*295*). Mercury-203 has been used as a radioactive indicator of the position of protein spots (*487*), and the staining of protein spots by mercuric ion followed by photography with ultraviolet light has been used (*48*).

Though the greatest use of paper electrophoresis has been for the separation of common proteins, it has found wide and successful application in the study of many other materials, both inorganic and organic, including protein materials of special function such as hormones and enzymes. Even those materials such as steroids and sugars that are not themselves ionic may be separated by altering them chemically, or through complex formation with ionizing materials. Included in the types of compound that are susceptible to separation and identification are nucleic acid derivatives (*110, 111, 121, 241, 510*); serum lipides (*132, 361, 423, 480*); carbohydrates (*100, 151, 204, 239, 415, 476, 531*); enzymes (*208, 298, 362, 366, 380, 490*); phosphate esters (*438, 439*); steroids (*498*); adrenocorticotropic hormone (*299, 306, 316*); plant viruses (*185*); serum hemochromogens (*209*); vitamin B_{12} (*444*); animal poisons (*360*); indole derivatives (*112*); serum iodine (*417*); α-keto acid dinitrophenylhydrazones (*359*); trypsin inhibitors (*238*); and other miscellaneous items of interest (*288*). Paper electrophoresis has been reviewed by several authors (*37, 307, 342, 521*).

COUNTERCURRENT DISTRIBUTION

The technique of countercurrent distribution continues to make significant contributions in the analysis of systems of biological interest. The relative costliness of the apparatus and the competition of the similar but simpler methods of chromatography have prevented the wide exploitation that so valuable a method would otherwise have enjoyed.

The conditions were determined and a technique was developed for the fractionation of insulin (*198*) which was used in a comparative study of insulin from different species (*199*). It failed to distinguish between various insulins, though the amino acid analyses were shown to be distinctive for the insulins from various species. Countercurrent distribution has been most valuable in isolating and studying certain hormones (*160*) including estrogens (*339, 464*) and adrenocorticotropic hormone (*78, 276*); antibiotics (*54, 104, 470*); flavins (*406*); porphyrins (*182, 388*); bile acids (*2*); polypeptin (*205*); and lipide materials (*1, 75, 76, 97, 98*), including phospholipides (*290, 370*). Modifications of apparatus have also been described (*335*) and the technique has been reviewed (*102*).

CELLULAR FRACTIONATION

The isolation procedures for morphologically "native" particles from cell homogenates have continued to advance during the 2 years since the previous review (*259*). Differential centrifugation is the necessary technique now, as it was even before 1948 when Hogeboom, Schneider, and Pallade (*441*) determined by microscopic control that isotonic or hypertonic sucrose solutions (ca. 0.2 to $0.9M$) were the preferred extraction media for mammalian cell fractionation. The various steps in the preparation of nuclear, mitochondrial, and microsomal fractions have not changed in essentials, although the newer Spinco preparative ultracentrifuge now permits more rapid treatment of larger homogenates.

As the criteria evolve, it becomes apparent that the isolation of the nuclei from cells may require a distinct technique, unsuitable for the simultaneous preparation of mitochondria, unless compromises in media are made. Thus, the use of millimolar concentrations of calcium ion "harden" nuclei (*440*) without aggregating cytoplasmic particles. Hogeboom *et al.* (*221–223*) prefer this medium and consider the idea is now definite that nuclear enzymic activity is generally due to contaminant mitochondria. Other authors prefer $2M$ sucrose solution without calcium ion (*4, 91*), the higher polyethylene glycols (*314*), or even nonaqueous solvents as centrifugation media (*5, 30*). The last-mentioned treatment is not calculated to maintain aqueous solubility of proteins, or the native spectrum of enzyme activity.

More intimate study of nuclear structure at various stages of cell division is now possible, using the cytochemical method developed by Mazia and Dan (*332*). By carefully chosen treatments, the mitotic apparatus of the nucleus of sea urchin eggs may be isolated in pure form, compared to any previous methods. The eggs are fixed at chosen times in cold alcohol-water mixture, and treated with hydrogen peroxide to oxidize —SH groups to —S—S groups, thus "vulcanizing" the protein of the mitotic apparatus. After these treatments, the other proteins of the cell are dispersed in detergent solution and discarded. The procedure is capable of control at all times, using phase contrast microscopy. Future developments along these lines should yield more detailed knowledge of chromosomal nucleoprotein and its changes in structure and composition during the various stages of cell division. The electron microscope may provide a means of examination of ultrastructure in the massive mitotic apparatus, after suitable thin cross sections are obtained.

The second cellular fraction, the mitochondria, is believed to incorporate vast enzyme assemblies for the performance of the citric acid cycle and for fatty acid oxidation, among others (*514*). Evidence accumulates that similar particles occur in bacteria (*352*) and also in plant specimens (*314*, *341*). Electron microscopy by Pallade in 1952 (cf. *223*) and later by Sjöstrand (*455*) has demonstrated that these particles possess a definite ultrastructure and a membrane.

Investigation of the large mitochondria from heart muscle of the rabbit or rat using the phase contrast technique (*200*) has shown characteristic changes in shape, refractive index, and rate of respiration; all changes occur as a function of the osmolar concentration of solute (sucrose or potassium chloride).

Slater and Cleland (*95*, *458*, *459*) and Cleland (*94*) have confirmed the previous work and extended it in a biochemical direction. These workers found that maintenance of activity of such mitochondrial preparations for enzyme study was possible, if the chelating agent, ethylenediaminetetraacetate (EDTA), were included in the medium, at a millimolar level (*459*). They presumed the action of the chelate-former was to prevent degradation of structure and function due to too high endogenous calcium ion levels. Utilizing media containing ethylenediaminetetraacetate, these workers examined the system concerned with oxidation of α-ketoglutarate, testing a number of variables. For this system, the mitochondria were most active when swollen to supranormal size (hypotonic media) and least active when shrunken by hypertonic media. Such work is highly interesting, but the enzyme systems are not yet described on a physical or structural basis. Much further work remains.

More recent approaches to the separation of mitochondrial specimens by centrifugation have indicated that a continuity of particle sizes may exist, called mitochondria on a cytological basis, but potentially distinct on biochemical bases (*365*, *378*). Considering these difficulties, others have suggested a process of fractionation by the use of density gradients, using sucrose or other solutes for both osmotic control and density gradient formation (*50*, *226*, *227*, *270*). Holter's group (*227*) proposes the use of Diodon-sucrose mixtures in order to establish a gradient with 1.30 as the upper density limit; these workers found that the mitochondria of Xenopus liver had a density of 1.10 to 1.20 in such media.

The microsomes, the smaller cytoplasmic particles, have been relatively neglected, as these units lack the respiratory enzyme systems. A hemochromogen similar to but not identical with the common cytochromes has been found in the microsomal fraction by Strittmatter and Ball (*478*). This chromogen is responsible for the "buff" color of the fraction. Holter *et al.* (*227*) find heterogeneity also in the microsome fraction from their liver preparation; a range of density of 1.25 to 1.30 is obtained by their technique. The groups using the density gradient fractionation have returned to horizontal rotation heads on their Servall (*50*) and Spinco (*227*) centrifuges.

Advances in this field are fundamental to the study of macromolecular assemblies as they occur in the cell (*413*). The rate of advance has depended upon the general use of cytological control procedures and the development of compatible media or conditions. Progress seems slow on a *yearly* basis, but is phenomenal for the postward period, with biochemical *growth* stemming from the sound biology of Claude, Harvey, and many others.

DETERMINATIVE METHODS

Because of the lack of new trends and major advances in the development and application of determinative methods, far less need be written on this subject than on preparative methods. In addition, many determinative procedures such as photometric scanning of paper chromatograms and electrophoretic patterns have been discussed in connection with these subjects.

ABSORPTIOMETRY

Absorptiometry, in one form or another, continues to be the method of choice for the largest number of constituents of biological interest. Those absorptiometric procedures that depend on formation of visible color with a constituent, and measurement of the light absorption of the colored material formed, are not discussed here. This would constitute an impossibly large and varied assortment of methods that cannot be treated systematically in small space. The general availability of excellent instruments has been a favorable factor in raising the level of reliability of absorptiometric procedures and practice with use of visible light.

Ultraviolet Absorptiometry. Absorption of ultraviolet light continues to be an important procedure because it has specific application to the determination of a number of biological materials, and it has shown itself to be adaptable to cytological investigation by means of the ultraviolet microscope (*38*). While the most important type of analytical application of ultraviolet absorptiometry has been to the study of nucleic acid systems (*134*, *305*, *450*, *451*), the great biological significance of these compounds has accented the method. Applied to cellular research, the nucleic acid compounds (260 mμ) can be studied by microphotometry (*16*, *153*, *367*, *502*, *513*) in the nucleus and other cell structures while the cell undergoes its normal functions, or in isolated cell structures (*294*). Because aromatic compounds in general absorb in the ultraviolet, and many aromatics or heterocyclics have key importance in biological phenomena, ultraviolet absorptiometry is useful for many other types of study. These should be aided greatly by the recent publication of compiled ultraviolet absorption spectra of aromatic compounds (*154*).

While the Warburg technique continues to provide basic respiratory data for enzyme systems, spectrophotometry serves as the most rapid and dependable means of estimation of products whenever they show different light absorption. Thus, the rise of concentration of reduced diphosphopyridine nucleotide (DPNH) is most easily determined by estimation of the increase of absorbance at 340 mμ (*292*). This spectral change occurs because of reduction of a particular bond of the nicotinic acid moiety present in diphosphopyridine nucleotide. A similar optical change occurs during the reduction of the same bond in triphosphopyridine nucleotide. During combination of the diphosphopyridine nucleotide with its apoenzyme (alcohol dehydrogenase), a shift of absorption peak from 340 to 325 mμ was demonstrated (*486*).

Using thermostated cells and an ultrasensitive spectrophotometer (*89*) capable of simultaneous recording of absorption at several wave lengths *vs.* time, Chance and his coworkers (*86*, *87*, *90*) have been able to identify either transient intermediates in the metabolic reaction chain, or the steady-state concentrations of the various cytochromes. The most sensitive spectrophotometric method has been applied to bacterial and yeast cells, with the hope that the absorbing enzymes and coenzymes may be estimated under a variety of metabolic conditions (*88*).

Indirect measurements of coupled enzymatic reactions frequently involve the measure of reduced pyridine coenzyme (DPNH or TPNH) appearance, using absorbance increments at 340 mμ. Thus, the quantitative evidence (*228*) for the enzymatic transformation:

Sedulose-7-phosphate + glyceraldehyde-3-phosphate →
erythrose-4-phosphate + fructose-6-phosphate

is provided by the identification of the erythrose ester by paper chromatography and by measurement of the triphosphopyridine nucleotide formed. The triphosphopyridine nucleotide added is reduced in amounts proportional to the fructose-6-phosphate formed, by known enzymatic steps.

The combination of coenzymes with their specific protein (apoenzyme) is also accompanied by spectral changes. Thus, the combination of riboflavin-adenine-dinucleotide (FAD) results in doubled absorption at 451 mμ and changes in the shape of the spectral curve (*350*). Combination of diphosphothiamine with an apoenzyme to form α-carboxylase is indicated by spectral changes near 290 mμ (*454*). The spectrophotometer is thus obviously a key instrument for the enzyme chemist, which added to a Warburg apparatus, a pH meter, water baths, and a storage freezer, constitutes his indispensable equipment.

A spectrophotometric determination of protein —SH groups has been proposed by Boyer (*47*) on the basis of changes in the absorption of *p*-chloromercuribenzoate after the aryl-mercuric mercaptide forms. The method has certain advantages in that pH, temperature, and time of reaction may be varied over wider limits than is possible with the amperometric or potentiometric determinations.

In addition to those determinations that are not easily supplanted by competitive methods, the spectrophotometer continues to perform routine absorbance measurements which may be utilized for the determination of protein (280 mμ) (*29, 55, 321, 345*), chromoproteins such as hemoglobin, amino acids (*430*), and other compounds of biological interest (*311*). Combined with paper chromatography, it was used to determine the terminal carboxyl group of ovomucoid (*390*).

Despite the wide interest in, and use of ultraviolet absorption measurements, there is still serious need for the development of simple and inexpensive absorption cells that would allow wider instruction and more general application of this technique. A number of instrumental developments that have occurred (*41, 103, 144*), and present availability of improved recording instruments and multiplier phototube photometers may be expected to advance the application of ultraviolet absorptiometry in the biological field. Recent trends have been summarized by Stearns (*471*).

Infrared Absorptiometry. The possible contributions of infrared absorption measurements to the study of biological systems have not been generally achieved, because of the general unavailability of proper instruments and information. The difficulty of measuring in the presence of water has also limited severely the application of the technique. The complex field of steroid chemistry has profited greatly by the application of infrared absorptiometric measurements (*219, 425*). This application should increase greatly as a result of the present availability of an atlas of steroid infrared absorption spectra (*122*). Infrared absorption has also found application in the study of porphyrins (*106*), lipide fractions of brain (*442*), various volatile substances (*357*), compounds related to lignin (*210*), and polyglucosans (*22*). It has been used to study the oxidation of linoleic acid (*256*), and to compare normal and neoplastic tissues (*516*), and polarized infrared has been useful in the study of fibrous proteins (*181*). It has also found numerous miscellaneous uses as in detecting colorless materials on chromatograms (*232*), and photographically, in locating electrophoresis boundaries (*340*).

MISCELLANEOUS CHEMICAL AND INSTRUMENTAL METHODS

In the final analysis, biochemical analysis may be as broad as analytical chemistry itself, and any technique that is useful may find application in the analysis of biological systems. Analytical chemistry ordinary leads in the development of new approaches and techniques, and the direction it moves indicates the probable direction of future progress in biochemical analysis. While no complete discussion of such progress is possible in this publication, it is not amiss to call attention to useful compilations of analytical methods that should be familiar to the biochemical analyst. Outstanding in this list is the series of Mitchell, Kolthoff, Proskauer, and Weissberger (*344*), the first volume of which is of significance because of its treatment of functional group analysis, a subject that must leave an imprint on biochemical research. While polarography has received only limited attention in the biological field, its potentialities are such that it should be available to the biochemist, which is readily possible through new publications (*268*). Instrumental analysis, which is already a large part of the analytical activity of the biochemist, has also been treated recently (*42*). Finally, it is in order to point to the increasing awareness on the part of clinical analysts that their methods must be more than empirical and often inadequate procedures adopted solely for speed. This very hopeful development is indicated by the appearance of the first volume (*412*) of a series that should go far in improving the general level of clinical analysis.

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Nucleonics

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THIS article reviews the publications of the past 3 years (*58*).

The most powerful new tool of nuclear science which is new to analytical chemistry still is the method of activation analysis. For instance, Debiesse (*30*) could determine as little as 0.5γ of cobalt in nickel by irradiation in a flux of 6×10^9 neutrons per second per square centimeter. This requires the use of either a cyclotron or nuclear reactor, which are still far beyond the financial capacity of most analytical laboratories. Fortunately, the services of the Oak Ridge National Laboratory for this kind of analysis have been opened to outside groups (*21*). For research purposes it is still more desirable for the analyst to perform his own analyses, because unexpected developments can be pursued immediately and not after a report from some distant laboratory. Lower cost neutron sources include radium-beryllium incorporating from 25 mg. up to 3 grams of radium, costing from $600 to $75,000, and producing neutron fluxes of from 10^2 to 10^6 neutrons per sq. cm. per second. Antimony-beryllium sources are available for about $150 for a flux of up to 10,000 neutrons per sq. cm. per second, but have a 60-day half life. The chart of activation cross sections as a function of half lives of the radioisotope produced was given by Meinke and Anderson (*101*) and can be used as a guide as to the possibilities of the method.

METHODS OF ANALYSES AND SEPARATIONS

Activation Analysis. A review of the methods for determining the naturally occurring radioelements and the stable elements was given by Süe (*141*). Elements that have been determined in this manner are: antimony (*78*), boron (*141*), bromine as bromide (*151*), cadmium (*141*), carbon (*28*), cerium (*141*), cobalt (*3*), copper (*2*, *3*), indium (*101*), lithium (*141*), manganese (*3*), nickel (*3*), rhodium (*101*), silver (*101*, *141*), tantalum (*35*, *88*), thallium (*31*), yttrium (*141*), zirconium (*79*), and uranium (*67*).

Meinke and Anderson (*101*) made a study of the use of low level neutron sources (about 100 neutrons per sq. cm. per second) for precise activation analysis. From a study of the thermal neutron activation cross sections and the half lives of the products of the activation, they suggest that only rhodium, iridium, indium, silver, and dysprosium can be detected by this method. They give the errors of estimation of 1% of silver, rhodium, or indium in a mixture as about 6.7, 4.8, and 3.6% probable errors, respectively. The pile method of activation analysis is said to be able to determine as little as 7×10^{-9} gram, with an accuracy of 10%. Samples can be analyzed for impurities by the pile method by arrangement with Carbide and Carbon Chemicals Corp. (*103*).

Activation analysis has been used by Herr (*75*) to determine the isotopic composition of lithium in lithium carbonate. Samples of the unknown and a standard sample are placed on a photographic plate, irradiated with neutrons, developed, and evaluated photometrically.

Indicator Analysis. Instead of measuring the activity of the element being analyzed, the element may react with some other radioelement or ion containing a radioactive element which can then be measured. Govaerts and Barcia-Goyanes (*59, 60*), used a solution of silver containing radioactive silver-110 to precipitate chromium as silver chromate. The activity of the precipitate then was directly related to the amount of chromium present by a standard curve. Molybdenum and vanadium were similarly determined. Goyanes and Serrano (*8*) determined aluminum, zinc, magnesium, and manganese by precipitation as the orthophosphate using radioactive phosphorus. Ballard, Stevens, and Zuehlke (*7*) used iodine-131 as radioactive iodide to convert the silver of a photographic image quantitatively to silver iodide and then determined the silver content by measuring the iodine-131 activity. Langer (*92*) used radioactive silver as an end-point indicator in argentometric titrations.

Carrier-Free Separations. The production and isolation of carrier-free radioisotopes were reviewed by Garrison and Hamilton (*42*). Hamilton and coworkers continued their series of publications on simple and quick separations with separations for: magnesium-27 from aluminum (*69*), cesium-185 and rhodium-183, and -184 from tungsten (*43*), beryllium-7 from lithium (*70*), scandium-44, -46, -47, and -48 from titanium (*44*), bismuth-204 and -206 from lead (*45*), manganese-52 from chromium (*71*), palladium-103 from rhodium (*52*), iron-59 from cobalt (*46*), chromium-51 from vanadium (*46*), platinum-191 and -193 from osmium (*47*), ruthenium-97 and -103 from molybdenum (*47*), thallium-200, -201, and -202 from mercury (*48*), lead-203 from thallium (*72*), rhodium-100, -101, -102, and -105 from ruthenium (*49*), iridium-188, -190, and -192 from osmium (*73*), gold-195, -196, -198, and -199 from platinum (*50*), and tungsten-188 from tantalum (*51*).

The chemical separations of fission products were summarized by Wilkinson and Grummitt (*149*), and many papers on the individual separations are given in the volumes on the fission products of the National Nuclear Energy Series (*26*).

Other Separations. The Szilard-Chalmers effect is utilized for preparing many carrier-free radioactive isotopes. The method, however, is not an analytical one, in that the separation is not complete (*83*). An innovation to the ion exchange separation was introduced by Berne (*11*) for the separation of bromide ions from bromate. The exchanger was silver oxide–coated diatomaceous earth, from which the bromide was eluted with a soution of sodium iodide and barium ions. The silver and barium ions were removed by another ion exchanger. One of the simplest preparations of carrier-free isotopes was the production of a mixed solution of radiolead and radiobismuth. Broda *et al.* (*17*) caught thoron, in air bubbled through a concentrated solution of thorium nitrate, in 0.1*N* hydrochloric acid which then decayed to lead-212 and bismuth-212.

Chemla and Süe (*22*) were able to enrich sodium-22 from a mixture of sodium-22 and sodium-24 as the chloride by depositing them on a crystal of sodium chloride and causing them to migrate under an electrical field.

Barrett (*9*) studied the effect of an electric field on the collection of radioactive ions of bromine, technetium, and indium. After elimination of the radioactive ions carrying a negative charge, positive ions of bromine-80 produced by isomeric transition from boron-80* were collected on the aluminum windows by applying several hundred volts per centimeter potential to it. In analyzing aerosols for radioactivity, Pauthenier and Challande (*116*) used an electrical method similar to the Cottrell dust precipitator to precipitate all the radioactive particles. A reverse innovation has been the work of Linder (*94, 95*) and Ohmart (*115*) where the radioactive material has been used to produce a potential difference between two electrodes.

MEASUREMENT

Counting. The measurement of radioactivity usually involves counting in some form. There is statistically an optimum distribution of the minimum counting time between each sample counting rate and the background counting rate which yields a required degree of precision. A quick solution of the equations is given by Browning (*19*) in the form of easily used charts.

Among the methods of presenting the radioactive material to the counter for analysis is the measurement from the surface of a solution. Goddu and Rogers (*56*) compared the count from solutions of silver in a lacquered aluminum dish with that from the same solutions in glass cups. The activity of the former decreased because of the plating out of the silver-111 from the solution onto the lacquer. Evaporation of liquid caused the activity of the latter to increase with time and showed the necessity of control of evaporation. Freedman and Hume (*40*) overcame the evaporation losses by covering the liquid with a thin film of lacquer. Preparation of coated foils was presented by Dodson *et al.* (*33*). Spevack (*135*) applied for a patent on the method of introducing the radioactive material into an organic base which, after spreading on a foil, can be completely burned off, leaving the isotope as a compound of known composition.

A comparison of counting methods used in determining iodine-121 was made by Bruner and Perkinson (*20*). They found the flow-gas type of proportional counter gave the highest sensitivity, but wet sample procedures give simpler and more stable counting systems.

Filtration of the precipitated radioactively labeled material onto a glass frit with low shoulders was used by Pinajian and Cross (*117*). A minimum "infinitely thick" sample is prepared. Dry solid particles such as ground rock or mineral were counted by Kulp (*90*) as a thick source with a sample tray filled to 2.7-mm. depth or as a thin source where the material was ground to pass a 300-mesh screen and dusted onto a silicone-grease–coated sample pan. The reproducibility of these films was within the statistical error of counting. A thin nylon support was used by Baker and Katz (*6*) to minimize back-scattering.

Dust samples are usually collected by impingement on filter paper and the radioactivity measured by direct counting of the surface. Alercio and Harley (*4*) found that penetration into the paper reduced the α-counting efficiency 30%, because of absorption of these particles by the paper. Siksna (*134*) determined variations in the ion content of air by making autoradiographs of the deposit collected on a brass disk when at a negative potential of 4.5 kv. for 8 hours.

Another method of presenting a solution in a flat surface to the counter was devised by Sear (*127*). He used a flat coil of thin-walled small-diameter polyethylene tubing to contain the solution. Raben and Bloembergen (*119*) introduced radioactive carbon in the form of soluble compounds directly into a liquid scintillator contained in a cell between two photomultiplier tubes. About 25% of the disintegrations were counted.

For the standardization of counting, laboratory standards are usually prepared. Several methods for making stable reproducible standards have been given (*114, 132, 133*).

Schweitzer and Nehls (*126*) recommend that each investigator prepare his own correction curves for self-absorption. The self-absorption factor, *F*, for various β-ray emitters has been computed by Nervik and Stevenson (*113*) as a function of the sample thickness. Other data on self-absorption and back-scattering have been obtained (*23, 36, 37, 55, 66, 85, 125, 130*).

Photographic Techniques. Half lives can be determined photographically (*120*) by determining the activity by contact autoradiography at different times during the decay of the material.

Neutron flux densities were measured by loading the nuclear emulsion plate with boron-14 and lithium-6. Evaporating a solution of these isotopes in the form of lithium borate is used to obtain a high concentration of them in the emulsion. Haenny and Klement (*65*), using this technique and also loading the emulsion separately with the lithium or boron, determined their relative cross sections.

Kaplan and Yagoda (*82*) used this technique for determining the neutron flux produced by cosmic radiation (neutron background) which they found to be about 230 slow neutrons per square centimeter per day. They suggest the use of this method for purposes of health monitoring.

Braun (*16*) studied the factors affecting the length of the tracks in nuclear emulsions and found that an error of not more than 0.5% was practical. Loading the plates affects the track length unpredictably. Shrinkage in the emulsion gives rise to a necessary correction in the track length. This shrinkage factor was found by Horan (*77*) to be a function of the angle of incidence and the usual correction should be restricted to angles of dip of less than 6° if the error of measurement is to be less than 2%. The horizontal α-ray ranges alone were found by Poole and Matthews (*118*) to be usable as a means of determining thorium-uranium concentration ratios. They used the ratio of the number of tracks per square centimeter with horizontal ranges exceeding the maximum range of RaC′ to the number of tracks with horizontal ranges between the maximum range of RaC′ and the maximum range of ThA.

For testing the resolution of autoradiographs, Stevens (*137*) toned photographic resolution test charts to convert the silver to silver iodide, with the latter containing iodine-131. Coating such charts with layers of known thicknesses of gelatin gives measurements on the loss of resolution when the radioactivity is located beneath the surface as in histological specimen. Three microns separation seriously reduced the sharpness of the image. Gomberg (*57*) claimed that the resolution of the wet process emulsion was about 1 micron and used a technique of producing the emulsion on the radioactive specimen. Rasch (*121*) used an emulsion-coating technique to render visible the radioactive centers of alloys.

A method for the discrimination between particle tracks and fog (as by gamma radiation) is by underdevelopment. Gailloud and Haenny (*41*) found that by choosing a surface developer and adjusting the pH, by the addition of acetic acid, to as low as 6.8 would give discrimination against γ-ray fog produced by 200 roentgens. Cosyns, Dilworth, and Occhialini (*27*) measured the effect of lowering the temperature on the sensitivity of nuclear emulsions with the intent to eliminate cosmic-ray tracks appearing in stored film. Significant but not complete elimination was observed.

For weak sources of radioactivity Ader (*1*) immersed a capillary tube containing the sample in a liquid photographic emulsion. The number and length of the tracks after development were used to determine the amount of radioactivity. Walker (*144*) analyzed high-energy protons by means of a stack of photographic plates separated from each other by thin aluminum foils.

MISCELLANEOUS TYPES OF DETERMINATIONS

Pressure, Temperature. Ecker (*34*) used mercury-203, producing its γ-emitting daughter thallium-203, to measure the density of the mercury inside a mercury arc. Then knowing the pressure, he determined the temperature from the gas equation of state. Conversely, Dainton and Kimberley (*29*) used the activity of phosphorus-32 to determine the vapor pressure of white phosphorus at a given temperature.

Solubility. A double precipitation method of determining the solubility of a compound with radioactive indicators was published by Neiman *et al.* (*112*). In one example they precipitated copper thiocyanate in a 50% solution of zinc sulfate at 20°, with copper-64 as the indicator. The procedure in the simplest form is as follows:

> To a solution containing a millimoles of inactive ions A and an unknown amount of radioactive ions A with an activity of c counts per minute, add the reagent D necessary for the precipitation of the compound B of unknown solubility and bring the volume of the solution to v ml. Then filter off and determine the activity of the precipitated compound as i_1 counts per minute. To the filtrate which contains the activity representing the solubility of B, add a millimoles of inactive A and the reagent D and again bring the volume to v ml. (evaporation). Again filter off this precipitate and determine its activity as i_2. If the unknown solubility is x millimoles per milliliter, the amount of B remaining in solution after the first precipitation is xv millimoles and the amount in the precipitate is $(a - xv)$ millimoles. The activity of the first precipitate is $i_1 = C(a - xv)/a$. After the second precipitation the solution again contains xv millimoles of B and the precipitate contains $(a + xv - xv) = a$ millimoles of B. The activity of the second precipitate is $i_2 = cxv/(a + xv)$. The absolute activity of the two precipitates is not found but, their ratio, $i_1/i_2 = \beta$, can be easily determined and the solubility $x = a(\sqrt{\beta^2 + 4} - \beta)/2v$.

Surface. Hershenson and Rogers (*76*) studied the errors in volumetric analysis arising from adsorption using a 50-μl. Kirk pipet. They found that the percentage of the silver introduced into the pipet and adsorbed on its walls increased from about 0.25% with $1M$ silver solution to 1.7% with $10^{-6}M$ solutions. An ordinary 1-ml. pipet having nearly the same ratio of surface to volume gave values which agreed with those of the 50-μl. pipet. Long and Willard (*97*) extended their previous work (*74*) on the sorption of ions on soft glass to determine whether the sorption process is a simple exchange process. Using sodium-24 (15-hour half life) as a preliminary adsorbed ion on soft glass and then immersing in sodium-22 (3-year half life), they were able to determine that the amounts sorbing and desorbing with time were approximately constant, though not necessarily at equal rates. To study the leaching of sodium directly from the glass, they irradiated the 1-inch square glass specimens with thermal neutrons and found that the fraction of sodium leached from its surface by $0.1N$ nitric acid (water was nearly equally effective) was approximately 1.1×10^{-5}.

Willard (*150*) reports the results of tests of bromine vapor in contact with glass, in which it was found that ordinarily a monolayer of bromine was attached to the glass after 30 minutes, but if the exposure was conducted at a higher temperature, 150° to 175°, three times as much bromine was adsorbed. The bromine remained on the samples even after evacuation for half an hour and standing in air for 24 hours.

Beischer (*10*) used carbon-14–tagged stearic acid monolayers to apply radioactive tracer to the surface of various materials. On heating and causing thermal diffusion on the surface, different amounts of chemical reaction of the stearic acid with various parts of the surface are caused by variations in the structure of the surface. Radioautographs of the surface can be taken and the quantitative amount of activity determined. The opposite technique of making the metal radioactive and applying the stearic acid to it was used by Bowden and Moore (*13*).

Westermark and Erwall (*148*) used autoradiographs of the preferentially sorbed phosphorus-22 or lead-217 on minerals to outline phase areas and noted that lead has a higher sorption of lead-217 than has antimony.

Milutinovic and Novakov (*102*) studied the surface areas of powders by comparing the amount of iodine exchanged with the powder and the amount of iodine exchanged on the powder material when fused into small spheres of determined surface area. A slight difference was noted with iodine-128 as an indicator when a maximum of 66% of the chlorine in lead chloride was exchanged with potassium iodide, whereas with untagged iodine the maximum was 64%.

Isotopic Effects. In studies on the relative rates of hydrolysis of urea Schmitt, Myerson, and Daniels (*124*) found that of the isotopes of carbon, carbon-14 reacted the slowest and carbon-13 more slowly than did carbon-12. The carbon-14, and to lesser extent carbon-13, accumulated in the last fraction to decompose. Stevens, Pepper, and Lounsbury (*138*) found the carbon-14 effect to be more than double the carbon-13 effect. Lindsay, Bourns, and Thode (*96*) found the probability of the rupture of a carbon-12–carbon-12 bond to be 2% greater than that of a carbon-13–carbon-12 bond. Gilman, Dunn, and Hammond (*53*) found a very large difference in the silicon-hydrogen bond. When the normal hydrogen and the deuterium compounds of Ph_3SiH were hydrolyzed, the deuterated compound reacted nearly six times faster than the normal.

Isotopic Exchange. Harris (*68*) analyzed the rate characteristics of isotopic exchange and noted that the influence of the isotope effect is determined by the exchange mechanism. Karamyan (*83*) studied the Szilard-Chalmers method of separation of radioisotopes made by the (n, γ) reaction, and found that there is not complete separation.

SAFETY

Considerations regarding the safety of the analyst using radioactive isotopes involve: removal of deposited activities from contaminated surfaces, such as the apparatus used or the person of the analyst; removal of activities from the air; removal of activities from the laboratory wastes; and protection of the analyst from the radiations during the analysis.

Surface Decontamination. One method of removing the residual surface activities after using apparatus is by coating the apparatus with a strippable film such as paraffin as used by Beischer (*10*). The other method is to remove the activities by chemical treatment. DeMent (*32*) sprayed the surface with a solution of sodium trisilicate. On converting this to silicic acid by application of hot mineral acid followed by washing with water, the contaminants were removed. Künkel (*89*) tested a number of cleaners and found silicon tetrachloride especially effective for noncorrodable surfaces. For removal from the skin, a mixture of titanium dioxide and a weak solution of hydrochloric acid was effective.

Gregory (*62*) found a mixture of powdered wood and soap powder effective in removing substances containing uranium and radium from the hands. The Subcommittee on Waste Disposal and Decontamination has prepared a handbook on decontamination in laboratories (*106*). For very difficultly removable hand contamination immersion in strong hydrochloric acid for a short time is feasible, provided there are no scratches or other lesions in the skin. Tompkins, Bizzell, and Watson (*142*) tested various methods of removal using radioactive phosphate, barium, and iodide solutions.

Waste Disposal. The Subcommittee on Waste Disposal and Decontamination of the National Committee on Radiation Protection has prepared several handbooks in this field. The handbook on recommendations for waste disposal of phosphorus-32 and iodine-131 for medical users (*107*) gives calculations on the permissible amounts of these activities which may safely be disposed to the sewer. Sample calculations for this type of disposal were also given by Kittrell (*86*).

The sewage must be treated to remove or reduce the permissible amounts of radioactive isotopes allowed to pass into the effluent. Ruchhoft and others (*122*) studied the use of food wastes to support zoological organisms which remove radioactive elements by adsorption. They (*123*) found biological methods remove only 95% of the activity. Grune and Eliassen (*63*) noted that phosphorus-32 in concentrations of up to 10 mc. per liter did not affect the biological oxygen demand value. Ruchhoft (*123*), however, says that biological treatment is not satisfactory for the removal of phosphorus-32, which is isotopically diluted by the constituents of sewage nor is it applicable to soluble isotopes that are not utilized or readily adsorbed on the biological floc. The detection and determination of the amount of radioactive materials in waste streams were discussed by Fields and Pyle (*39*) and by Kochtitzky and Placak (*87*).

Other methods of waste disposal involve concentrating and storage. It has already become necessary to increase the storage capacity for radiochemical wastes and this has been accomplished by reducing the volume of the wastes by means of a 300-gallon-per-hour evaporator as described by Browder (*18*). McCullough (*99*) extends the evaporation to reduce the solids to a 5 to 10% moisture content.

Ion exchange is another method of concentrating the radioactive wastes. Ayres (*5*) studied this method and noted a further increase in concentration by a factor of 16 on ashing the organic exchangers. Machis and Geyer (*98*) noted that ashing of phosphorus-32 residues can be expected to produce an ash of sufficiently high activity to constitute a dust hazard in some instances. A review of radioactive-dust removal equipment was given by Bralove (*14, 15*). Corey, Perry, and Schwartz (*25*) used a gas-cleaning system together with a molten flux of sodium hydroxide under the grate in an incinerator to concentrate the wastes in an easily disposable solid matrix.

Decontamination of waste water solutions and decontamination of drinking water are essentially the same problem. Lacy (*91*) used powdered metal slurries to adsorb the radioactive materials to a safe tolerance level for drinking purposes after coagulation and filtration. A method for electrodialyzing solutions to separate wastes, including radioactive materials, was patented by Juda and McRae (*81*). Filtration systems for decontaminating water are described, among others, by Lauderdale and Emmons (*93*) and by Straub (*139, 140*).

Standards. A method of making Geiger-counter measurements in the calibration of a large number of standards, which reduces the time required by 70%, was reported by Seliger (*129*). The method utilizes the statistical technique of the Latin square. $4\text{-}\pi$ counting in the standardization of radioisotopes by pill box, spherical, and cylindrical counters was studied (*131*). These different counters agreed within 1%. Neglect of the fractional back-scattering from thin films was found not to affect the accuracy limits of this method (*100*). For such low-energy β-emitters as cobalt-60 extreme precautions are required to eliminate self-absorption errors.

General References. A number of texts of interest to analysts working with radioactive chemicals appeared during the past 3 years (*12, 24, 26, 38, 54, 61, 64, 80, 84, 104, 128, 135, 143*).

Three supplements to the collection of nuclear data have been published (*145–147*). The safety limits for personnel protection are being summarized by the National Committee on Radiation Protection and published as handbooks by the National Bureau of Standards (*105–111, 152*).

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[End of Review Section]

Literature Problems in Analytical Photometry

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As a result of many decades of work, the chemist now possesses a considerable number of different kinds of analytical methods, by means of which he has been able to accumulate a wealth of information concerning both the qualitative and the quantitative composition of vast numbers of substances. Classical examples of such procedures are the widely known processes of gravimetry and titrimetry.

Another of these processes, now also widely used, is absorptiometry. In this type the physical property measured is the capacity of a given sample system to absorb radiant energy. Because the literature for this area is extensive, fairly involved, and widely scattered, it has seemed worth while to present some of the library problems encountered by the author during more than two decades of such work.

A note of explanation of the methods may help in understanding the nature of the literature relating to them. First of all, the word "absorptiometric" is used in a general way to include two different types of procedures based upon the absorption of radiant energy.

The first kind may be designated as comparometric, since a quantitative determination consists in comparing the intensity of the color of the unknown with that of a standard. Generations of chemists have used the terms "colorimetry," "colorimetric," and "colorimeter" here, most often with reference to standard series and balancing techniques. Such usage usually disregards physicists' reservation of these terms for the measurement of color as color, without regard for the nature of the colorant or its amount.

The second kind may be designated as photometric, which includes the use of both filter photometers and spectrophotometers. With these instruments one actually measures, in percentage or some related term, the absorptive capacity of the sample for given wave lengths of radiant energy. As the spectral region of 0.2 to 25 microns is at present analytically most useful, the discussion is thus limited. Also, the emphasis is on photometry and its applications.

Like most other methods of chemical analysis, photometric methods generally involve both chemistry and physics. The chemistry concerns the transformations required to produce a system fit for measurement. Representative common operations and processes are fusion, dissolution, oxidation-reduction, complexation, volatilization, precipitation, extraction, electrodeposition, and adsorption. The physics concerns the final operation of measurement—that is, principles and uses of the photometers.

Much of the relevant chemistry has a long background. Spectrophotometers, in at least primitive form, go back nearly a century. Current applications have become very extensive and diverse. Consequently, only the general nature of the literature for each part of the total problem is considered. In general, the references cited are among the most important. If desired, they will lead the way to others.

CHEMISTRY

Few desired constituents can be measured as such in the usual environment in which they occur. The chemistry of concern to us is that which is applicable and necessary to make measurement possible.

In general, the kind of information needed, as far as it is collected and systematized, is to be found in the great treatises and in monographs. Subsequent to the time of their publication, one must turn, of course, to abstracting journals and thence to the original sources, such as periodicals, bulletins, and patents.

For the general chemistry of organic compounds and their reactions, the incomparable source is the Beilstein treatise (*43*). The newer Elsevier (*44*) and Grignard (*15*) treatises are valuable complements to the Beilstein set, as is the set by Heilbron and Bunbury (*17*).

As one turns from these comprehensive works to those more specialized, perhaps certain monographs are next in importance. Thus, the ring index of Patterson and Capell (*42*) serves for quick checking of particular structural types of organic compounds. Compilations such as those of Yoe and Sarver (*53*), Mellan (*34*), and Welcher (*51*) summarize much information on organic reagents. Still more specialized is Martell and Calvin's discussion of metal chelate compounds (*32*).

For inorganic chemistry the five treatises of most general value are those of Gmelin (*39*), Mellor (*38*), Friend (*12*), Pascal (*41*), and Abegg and Auerbach (*1*). There is often a long time lag in parts of these sets, the least serious perhaps being in the Gmelin set.

Useful works specifically analytical are the new Fresenius and Jander (*10*) and the relatively old Rüdisüle (*45*) treatises. The monograph of Hillebrand and Lundell (*19*) is invaluable in being critical and up to date.

The spectral range of 0.2 to 25 microns covers the nonvacuum ultraviolet, the visible, and the as yet analytically usable infrared regions. Very largely our interest in chemical transformations concerns the preparation of systems for measurement in the visible region—that is, colored solutions. Important requirements of such systems, and of reactions used for producing the solutions, have been summarized elsewhere (*36*).

A specific problem may emphasize the complexity of some of the chemical difficulties. Suppose one wishes to determine minor amounts of germanium in an alloy by photometric measurement of the heteropoly complex, molybdogermanic acid, or its blue reduction product. Assume, for simplicity, no interference by constituents other than possible small amounts of arsenic, phosphorus, and silicon, elements all likely to be present in trace amounts in many alloys.

As these other three elements also form heteropoly acids, one has at once the likelihood of a polycomponent absorbing system containing all four complexes. As their individual absorptive characteristics are too much alike to permit simultaneous photometric determination, we must "hitlerize" (divide and conquer) the system. Chemically this means to discover and take advantage of any small differences in properties that are applicable.

Various questions arise. What conditions, such as pH, affect the complexes? What is their stability under different conditions? Are they all colored? May they be selectively formed or reduced? Do they all form mixed acids, and, if so, are the properties all similar? If separations must be used, should the process (es) be applied before or after formation of the complexes? In either case, what is the possible applicability of common separative processes such as selective volatilization, precipitation, electrodeposition, liquid-liquid extraction, and adsorption? Only when the answers to these questions, and others of like nature, are at hand can the analyst decide what can be done chemically to obtain a system susceptible to satisfactory measurement. The over-all problem here is not easy, for heteropoly chemistry extends back at least a century and a quarter.

PHYSICS

Next one comes to the means of measurement—that is, photometers. This term is used to include both filter photometers and spectrophotometers. Sometimes the former are called abridged spectrophotometers, and the latter spectrometers. Many writers use the term "photoelectric colorimeter," instead of filter photometer, if the detector is a photocell. All this must be kept in mind in searching the literature, especially as some writers are not clear in usage of terms.

The distinction between the two types of photometers is one of degree, or refinement, rather than of kind. In general, filter photometers employ broad range sources from which a filter isolates and passes a band of wave lengths, which in extreme cases may be as much as half the visible spectrum in width. Spectrophotometers, in contrast, incorporate a prism or grating to disperse the radiant energy of the source and then a mechanical slit to isolate and pass the desired spectral band. Usually this band is between 1 and 100 A. in width. Ideally, perhaps, spectrophotometers should operate on monochromatic sources, but almost none do. No further attention will be given here to any differences between the instruments.

With the first spectrophotometer usually attributed to Govi (*14*) in 1860, the literature now covers nearly a century. Prior to 1900, references appear largely in journals on physics or closely related subjects. Few composite instruments were in chemical use prior to 1915. Assemblies consisted, in essence, of a source of radiant energy, a monochromator (or filter), a photometer, an absorption cell (for gases and liquids), and a detector. The literature concerns the development of a variety of each of these items, and their applications in different ways. Thus, 72 possible variations in spectrophotometric arrangements have been suggested (*22*). Many of the earliest contributions have been summarized by Gibson (*13*), Kayser (*25*), and Krüss and Krüss (*28*). The author's brief review (*35*) covering the century 1852–1952, concerns both types of absorptiometers for the visible region of the spectrum. Two monographs cite many historically important references (*5, 37*). Several other monographs present different viewpoints (*26, 31, 33*).

What is more important to the chemist today concerns current developments in instruments. New or improved devices come now from individuals having interests as varied as chemistry, biology, optics, electronics, and engineering. For all such items, then, one should be able to turn to abstracting services for the respective fields. In chemistry this means the general abstracting journals, *Chemical Abstracts*, *British Abstracts*, and *Chemisches Zentralblatt*. In biology it is *Biological Abstracts*, in physics it is *Science Abstracts*, and in engineering it is *Engineering Index*.

Selection of headings under which to search in subject indexes of such sources is important. The words "photometer" and "spectrophotometer" may be adequate, if complete instruments are described. More often some part of an assembly is concerned. Then one may need to have in mind specific items, such as; (1) sources of radiant energy, such as the hydrogen arc, different spectral lines, tungsten filament lamps, C.I.E. illuminants (*A*,*B*, *C*), Nernst glowers, and Globar lamps; (2) monochromators, both grating and prism types; (3) filters; (4) photometers, such as the polarization, rotating sector, iris, and neutral wedge types; and (5) detectors, such as the photographic plate (film), various kinds of photocells (photoemissive, photovoltaic, photoconductive), the human eye, thermocouples, bolometers, and oscilloscopes.

To these more or less standard parts should be added, for particular instruments, certain special attachments. Illustrative of such accessories are indicators, recorders, multiple-ordinate plotting cams, and automatic integrators for tristimulus calculations.

All of this means, of course, that the searcher must be alert to all such instrumental details to avoid missing important headings in subject indexes. Even then, the specialist in photometry may profit from the expert advice on searching by E. J. Crane, editor of *Chemical Abstracts* (*7*).

Another point of interest in this connection may be mentioned. Because of lack of agreement on nomenclature, entries likely to be important for instruments are photometers, spectrographs, spectrometers, spectrophotometers, and spectroscopes. Those dealing more broadly with the subject are photometry, spectrochemistry, spectrography, spectrophotometry, spectrometry, spectroscopy, and spectrum (absorption).

Because wide appreciation of photometry as an analytical technique is fairly recent, one cannot be sure, especially in the older literature, that chemical journals carry abstracts on such instruments.

All of these difficulties apply to annual and cumulative subject indexes of abstracting journals. There is still more difficulty for one trying to follow developments during a current year. For an example, we may consider the use of *Chemical Abstracts*. As it has no issue subject index, each number must be read. For photometers, both filter and spectro-, the author examines regularly the following sections; 1. Apparatus, Plant Equipment, and Unit Operations; 2. General and Physical Chemistry; 3. Electronic Phenomena and Spectra; and 7. Analytical Chemistry. An occasional reference may be located elsewhere.

These abstracts cover journals, governmental bulletins, and patents. Occasionally manufacturer's technical publications, which are not abstracted, appear long before any technical description of the instruments. Advertisements must be watched for such information. Also anyone interested should keep his name on the mailing lists of companies in the field.

APPLICATIONS

The application of photometers is considered only from the viewpoint of their concern to analysts. Broadly speaking, the three main analytical uses are qualitative analysis, quantitative analysis, and the determination of absorptive data as such. Inasmuch as Vierordt (*50*) is given the credit for the first analytical use of a spectrophotometer, in 1873, the work now spans eight decades.

Chemical Analysis. The absorbing power of a selectively transmitting solution has both qualitative and quantitative aspects. Let us assume an absorption spectrum of the system in the form of a curve having absorbing power as the ordinate and spectral region covered as the abscissa. Then the form or profile of the curve characterizes the system qualitatively; and the vertical position of the curve, with respect to the x-axis, characterizes the system quantitatively.

The laws of absorption for such a solution may be summarized in the expression,

$$\log_{10} 1/T = abc = A$$

in which T = transmittance, a = absorptivity, b = thickness, c = concentration, and A = absorbance.

Library difficulties arise at once because of diverse usage in the literature, such as definitions, symbols, manner of plotting curves, and specifications of conditions of measurement. Usually the abscissa of curves give the spectral region covered, but the designation may be wave length (μ, mμ, or A.), wave number, or frequency. Some are $\log_2$ of wave length (mμ). The ordinate may be transmittance (T), per cent transmittance ($100\ T$), absorbance (A = extinction, E = optical density, D), absorptance ($1 - T$), molar absorptivity (a_M = molar absorbance index = molar extinction coefficient, ϵ), or log of molar absorptivity. Occasionally one cannot be sure that an ordinate labeled absorption is not really transmittance. Usage may even be inconsistent in the same paper.

When it comes to a physical constant, such as molar absorptivity, all factors affecting variability should be clear. Some examples for solutions are concentration, cell thickness, temperature, solvent, spectral band width, and wave length of measurement. Many current papers are analytically inadequate in this respect. It should be obvious that one unaware of the importance of all such details is hardly in a position to evaluate the significance of papers in this field.

Actual preparation of a sample for measurement is generally just as much of a problem as for other kinds of methods. The alert searcher should be aware of the necessity of the requisite preparative processes and operations.

Primary sources, such as periodicals, bulletins, and patents, contain increasing amounts of such information. Sections 2, 6, and 10 of *Chemical Abstracts* are most important in a general way; but many others, especially Section 11, should not be overlooked. A number of treatises and monographs, already mentioned, deal with such chemistry. In all of them the primary concern is the preparation of colored solutions. No comparable compilations relate to systems for measurement in the ultraviolet or infrared regions. In fact, little work has been reported dealing with the formation of specific compounds for measurement in these regions.

The great wealth of information on applications consists largely of specific methods for given materials. Thus, one finds the ASTM all-photometric methods (*4*) for the minor constituents in magnesium alloys, and the APHA colorimetric methods (*3*) for a score of constituents in water analysis.

The most comprehensive general compilation of such methods is by the Snells (*47*). A dozen other works cover less ground and may be more specific (*8, 9, 16, 18, 20, 21, 27, 30, 40, 46, 49, 52*).

The relative importance of the applications of photometric methods becomes most impressive when one follows current periodicals. The author recently compared (*35*) absorptiometric methods for the visual region with titrimetric and gravimetric methods. The change in two decades is noteworthy. An extensive bibliography (*48*) covers selected methods employing photoelectric instruments.

Searching subject indexes of abstracting journals for such methods presents more difficulties. One needs another list of index headings and modifiers, such as ultraviolet, visual, and infrared. For the visual region the words "colorimetric," "colorimetry," and "colorimeter" may be best. Along with these may be needed the whole range of kinds of materials, such as steel, water, and petroleum products, as well as specific desired constituents, such as iron and silica.

In this kind of searching a particular difficulty concerns the lack of suitable naming or classification of analytical methods. As an illustration of what this deficiency means, the fourth decennial index of *Chemical Abstracts* may be taken as an example. Under the heading, "Nickel, detn.," are 70 entries, and under the heading, "Nickel, detn. in, steel," are 60 entries. In no case is there anything to indicate which of perhaps a half dozen methods of measurement is described. Thus, if one wants only the absorptiometric methods, all abstracts must be checked. The abstracts thus found may yield the desired information, although often they do not. The only recourse, then, is to consult the original publications.

Then following the current issues of *Chemical Abstracts* for the chemistry of such methods and their applications is even worse than for instruments alone. One reading the 33 divisions, in order, usually finds nothing in Section 1, and only a small number in Section 2. Section 3 has many, especially on the absorptive nature of systems in the ultraviolet and infrared. Section 3A yields little. Section 4 may include strictly analytical papers, but there is not much probability of any in Section 5. Sections 6 and 10 are of fundamental chemical interest.

Section 7, Analytical Chemistry, is the principal source for general methods and often for applications to specific materials. Unfortunately, one cannot depend upon cross references here for relevant work in other sections. It seems that the number of these citations might well be greatly increased.

Sections 8, 9, 11, and on to 31, deal primarily with some aspect of applied chemistry, but papers strictly analytical in nature may be included. Excellent examples are Sections 11B and 14. Mostly such papers are not cross indexed in Section 7. In view of this situation, the only way to avoid missing references is to examine practically every abstract of each issue.

Often titles are irksome in being noncommittal on the kind of method. Thus, expressions such as a micromethod and a method for trace amounts reveal nothing as to whether the procedure is photometric.

One concerned with qualitative aspects of absorption spectra has great interest in collections of data, such as tabulations giving the wave lengths (frequencies, wave numbers) of the peaks of absorption bands and spectrophotometric curves. Brode (*5*) has cited references to the older collections.

Three new American collections are significant. The one published by Friedel and Orchin (*11*) includes ultraviolet curves for 579 aromatic compounds. Curves covering the infrared region and also the ultraviolet in many cases, for many organic compounds, have been issued in loose-leaf form under sponsorship of the American Petroleum Institute (*2*). A noteworthy cooperative effort is the joint project of the National Research Council, the National Bureau of Standards, and the American Society for Testing Materials. The most useful infrared characteristics of many hundreds of organic compounds are being coded on IBM cards under the general direction of Kuentzel (*29*).

Color Analysis. An important use of spectrophotometric curves in the visual region of the spectrum is to designate the color of a system. The curve itself is considered fundamental. Conventional plotting is transmittance (for transparent systems) or reflectance (for opaque systems) as the ordinate *vs.* wave length, in millimicrons, as the abscissa. In 1931 there was international agreement to use such curves as a basis for calculating the C.I.E. trichromatic specification of a color in terms of three selected stimuli (*6*).

Two recent monographs summarize this broad and involved subject and include valuable bibliographies. The first (*23*) is the famous report of the colorimetry committee of the Optical Society of America. The second (*24*) is the result of a quarter of a century of work on color at the National Bureau of Standards.

Table I. Number of Periodicals with 1 to 5 References Each

References per Journal	No. of Journals	No. of References
1	88	88
2	19	38
3	9	27
4	9	36
5	5	25
Total	130	214

Table II. Periodicals with More than 5 References Each

Name	No. of Journals	No. of References
Analyst	1	21
ANAL. CHEM.	1	127
Anal. Chim. Acta	1	11
J. Am. Chem. Soc.	1	26
J. Chem. Soc. Japan	1	9
J. Opt. Soc. Amer.	1	22
Magyar Kém. Folyróirat	1	8
Z. anal. Chem.	1	12
Total	8	236

Table III. General Distribution of Kinds of Publications

Publications		No. of References
Kind	Number	
Periodicals	138	450
Patents	7	7
Books	11	11
Manufacturers' technical publications	16	16
	Total	484

DATA ON A REVIEW ARTICLE

The literature for most specific analytical problems will vary because of differences in nature, objective, and other factors. However, a general idea of the type of literature involved in photometry is illustrated by a review just completed by the author. This review covers advances made during a 2-year period for the analytical applications of absorptiometry in the visual region of the spectrum.

Tables I, II, and III summarize certain data for the 484 references selected as representative examples. A few items are of special interest. Thus, one journal has more than 25% of all references, and eight of the 138 journals cited have nearly half of the total number of references. The journals listed in Table II include four for analytical chemistry, three for general chemistry, and one for physics. Of the seven patents one is for a method of analysis (a process) and six are for instruments (machines). The books, either new or new editions, relate to the field reviewed. The manufacturers' technical publications are all for instruments and are not abstracted in *Chemical Abstracts*. There are no governmental bulletins.

To locate this material *Chemical Abstracts* was indispensable. The *News-Letter* of the Inter-Society Color Council was of value for some borderline material. Some references came from general reading, and a few were suggested by fellow workers in the field.

CONCLUSION

These comments obviously reflect one individual's experiences in his efforts to follow developments in one division of analytical chemistry. Without the kinds of publications mentioned, both original and secondary sources, the problem of keeping up to date would be too formidable to continue. With them one needs knowledge of the subject, including its peculiarities, along with skill in the art of searching. Finally, perseverance is indispensable, not only in collecting references, but in selecting from them relevant desired details.

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Kjeldahl Method for Organic Nitrogen

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THE extent to which the Kjeldahl method has been applied to organic analysis has led to the publication of many data. From time to time, reviews (*14*, *16*, *66*) have been published covering both macro- and micromethods. Comprehensive reports on microchemical methods have been made by Willits and Ogg (*71*, *72*). In a previous paper (*9*), the method was reviewed from its inception to 1939. This report covers the period from 1939 to the present date.

The Kjeldahl method, through the efforts of countless workers, has been modified to include many types of nitrogen compounds, and given a much wider scope than Kjeldahl could have anticipated when he devised the method which was primarily to follow the course of protein changes in grain. The considerable use of the method arises mainly from the fact that it is a relatively uncomplicated procedure. The ease with which the determination can be made has undoubtedly led workers to look upon it as a possible cure-all for problems in nitrogen analysis. It is obvious, however, from published data, that all forms of organic nitrogen cannot be converted quantitatively to ammonia.

In order to correlate the available data, the method has been broken down into its component parts—digestion, catalysts, distillation, titration, etc.

DIGESTION

The Kjeldahl method (*27*) is a wet oxidation using concentrated sulfuric acid. Originally, sulfuric acid alone was used, but because oxidation under such conditions was time-consuming, particularly if large samples were used, the method was soon modified by the addition of potassium sulfate (*21*). With the advantage of a higher boiling point, oxidation was possible in a much shorter time. Ogg and Willits (*46*) measured the temperature of boiling digestion mixtures at six different points, and having a potassium sulfate concentration from 0.25 to 0.875 gram per ml. of acid. Using nicotinic acid, they found that results varied from less than 1% to 11%, and attributed this difference to the boiling temperatures or insufficient heating. Milbauer (*44*) also studied the acid digestion, using diphenylamine as a type compound with various additives, and found that a mixture of 25 ml. of sulfuric acid, 1 gram of mercury, 20 grams of ($K_2S_2O_8$) and 25 ml. of hydrogen peroxide gave complete conversion in 4 minutes.

In the determination of nitrogen in foodstuffs (*1*), a digestion mixture of 40 grams of sodium sulfate and 1.6 grams of copper sulfate per 100 ml. of acid is recommended, with a digestion time of 6 hours. For the microdetermination of protein in 50% glycerol (*51*), bromine is used as an oxidizing agent, supplemented by 30% hydrogen peroxide. Rosenthaler (*57*), who studied the formation of ammonia by oxidation of nitrogen-containing compounds, stated that the final conversion to ammonia is caused by hydrolysis. Quartaroli (*53*) considered the digestion to take place in two steps: oxidation of the organic matter, and reduction of all nitrogen to the ammonium salt. From his experiments with pure compounds, he concluded that when oxidizing action is weak and slow, the accelerating action of the oxidizing phase is slight. Strong oxidizing agents are injurious in the reduction stage, resulting in the loss of nitrogen. Powdered pyrolusite is recommended as the most useful oxidizing agent.

At one time or another, there has been controversy as to the use of perchloric acid in the Kjeldahl digestion. By many workers its use is considered hazardous. However, shorter digestion times, with no loss of nitrogen, are reported. Pepkowitz and Shive (*49*) advocated the use of perchloric acid as a wet digestion micromethod, and claimed that for very resistant materials, the digestion is approximately four times as fast as the official method of the Association of Official Agricultural Chemists. Kaye and Weiner (*26*), however, stated that low results with heterocyclic compounds were obtained, although no loss of nitrogen from ammonium sulfate was observed. Koch (*28*) reported its use in the digestion of grass, grain, and potato. In conjunction with selenium (*58*) for the digestion of soils and animal foods, it is said to reduce the digestion time from 4 hours to 15 minutes. On the other hand (*55*), it is reported that the method of Mallol (*39*), using this combination, gave good results with the hydrochlorides of aniline and ephedrine, but poor results with such compounds as asparagine, aspartic acid, acetanilide, antipyrene, and caffeine. Wicks and Firminger (*69*) discouraged the use of perchloric acid, particularly in the micromethod, because large losses are developed by the use of a so-called excess which may not be too apparent with a macromethod. It is an extremely powerful oxidizing agent and must be used with caution, particularly from the standpoint of loss of nitrogen either through formation and subsequent decomposition of ammonium perchlorate or oxidation of ammonium sulfate to nitrogen. Pepkowitz *et al.* (*48*) obtained good results on addition of 10 drops of perchloric acid after strong heating of the sample in concentrated sulfuric acid, and cooling before the addition.

Hydrogen peroxide, also, is used frequently in both micro- and macro-Kjeldahl determinations as an oxidizing agent. Various workers (*12*, *34*, *54*, *59*) report favorably on its use. Marquez and Allista (*42*) found that the use of potassium pyrosulfate in conjunction with hydrogen peroxide gives rapid oxidations.

It is obvious that by increasing the severity of the reaction, oxidation will be accelerated. Disregarding for the moment the effect of catalysts, this is accomplished by the use of oxidizing agents and by increasing the salt content, with the consequent raising of the boiling point. The advantage of increasing the amount of potassium sulfate used, other than shortening of the digestion time, is that in many cases theoretical results are obtained which are not possible with the use of the conventional

10 grams of potassium sulfate. This has been confirmed by various workers (*8, 32, 47*).

CATALYSTS

Numerous elements and their salts have been used as catalysts in the Kjeldahl digestion. Mercury, as the metal, oxide, or sulfate, is probably universally accepted as the most efficient. Its only disadvantage, if it can be considered such, is that it is necessary to precipitate the mercury before distillations, since it forms complexes with ammonia. The use of other catalysts, such as copper sulfate or selenium, eliminates this difficulty.

A great amount of work has been done on the use of selenium as a catalyst since Lauro (*33*) first reported it. Sreenivasan and Sadasivan have explained the catalytic effect of selenium (*64*), and also reported that addition of mercuric oxide increased the efficiency of the catalyst. The kinetics of the Kjeldahl digestion using no catalyst, selenium, copper, mercury, and selenium-mercury, have been measured by Schwab and Schwab-Agallidis (*61*), who, working with aniline, showed this reaction to be of the first order. A review of the literature on the use of selenium as a catalyst has been published by Seebold (*62*).

In the determination of nitrogen in leather, Baker and Shuttleworth (*2*) compared minimum digestion times and found that the catalyst efficiency was of the following decreasing order: mercury, selenium, copper, manganese. Lloyd (*36*), reporting also on the nitrogen in leather, found slightly higher results with mercuric sulfate–selenium as compared with copper sulfate, and a digestion period which was shortened as much as 75% by the use of the mixed catalyst. A comparative study by Korek (*29*) on the effectiveness of various catalysts showed selenium–copper sulfate was more efficient in promoting complete conversion to ammonia. However, theoretical results were not obtained with aromatic amines and heterocyclic compounds. Copper sulfate is a relatively slow catalyst, although the use of the anhydrous salt (*4*) increases the efficiency. A report of the catalytic activity of copper, cadmium, and calcium selenates by Dalrymple and King (*15*) on samples containing protein showed a shorter digestion time than with selenium alone. Losses occur on prolonged heating, and the authors do not recommend the use of selenates. According to Hiller, Plazin, and Van Slyke (*23*), only digestion mixtures containing mercury as a catalyst gave nitrogen values for proteins comparable to those obtained by the Dumas method.

Willits, Coe, and Ogg (*70*) in their study of the determination of nitrogen in refractory heterocyclic compounds, did not recommend the use of selenium. A certain amount of caution must be exercised, as losses occur when more than 0.25 gram of selenium is used as a catalyst (*10*). Tellurium (*24*) has been proposed as a catalyst, replacing selenium. Comparative results (*7*) showed it to be unsatisfactory, both alone and in combination with copper sulfate or ferrous sulfate. An evaluation of copper sulfate and mercuric oxide by Potts, Parkham, and Schafer (*52*) in the determination of protein in fish meal showed that slightly higher results were obtained with mercuric oxide.

DISTILLATION AND DETERMINATION OF AMMONIA

The preparation of the Kjeldahl digest for distillation is largely mechanical, and the manipulative details are generally at the operator's discretion.

The recovery of ammonia, however, has been approached from various angles—e.g., direct distillation, steam distillation, aeration, and elimination of the distillation (*40, 41*). Probably the most accepted macromethod is direct distillation of the diluted and alkalinized digest. The recovery of ammonia is rapid, most of it coming over during the first few minutes' boil. An hour's continued boiling is apparently sufficient to remove all traces of ammonia. As an illustration, prepared mixtures simulating the Kjeldahl digest and containing ammonium sulfate were distilled (*11*). The results in Table I indicate the recovery is complete in 45 minutes. However, safe procedure would dictate a 1-hour boil.

Alkali must be added carefully to the diluted and cooled digest to avoid loss of ammonia. Ynalvez (*73*) recommended an outside boiler, and the introduction of the caustic through the steam tube. Fridman and Komissarova (*19*) transferred the digest to a distillation flask and neutralized with 20% sodium carbonate, using methyl orange as an indicator. Further dilution and addition of sodium bicarbonate are made prior to distillation. Distillation and determination of ammonia have also been made by the use of a closed system (*6, 13, 68*) and subsequent direct titration. Minimum recovery has been reported to be 99.9%.

Table I. Recovery of Ammonia from Ammonium Sulfate

Sample, Gram	Distillation Time, Min.	% Recovery
0.1000	5	78.77
0.1000	10	89.96, 91.97
0.1000	15	98.63, 96.73
0.1000	30	98.78, 98.38
0.1000	45	99.97, 100.16
0.1000	60	99.98, 100.09

The possibility of entrainment and subsequent carry-over of alkali is reduced by a regulated boil, with such added substances as boiling chips, or zinc and paraffin. Further reduction is obtainable by the use of an efficient trap.

The actual determination of ammonia may be accomplished in several ways, the most common of which is distillation of the ammonia into a measured excess of standard acid containing a suitable indicator. In place of the standard acid, there is frequently used a solution of boric acid (*13, 20, 25, 37, 67*) designated by investigators as saturated, 2%, 4%, etc. Taylor and Smith (*65*), using a micro-Kjeldahl method, distilled into exactly 10 ml. of 4% boric acid, made up to a final volume of 150 ml., and determined the pH. From a previously prepared calibration curve, the per cent nitrogen can be determined.

A method which has found wide application is the so-called "formol titration" (*60*). This procedure, which eliminates distillation, is based on the following reaction with formaldehyde:

$$2(NH_4)_2SO_4 + 6HCHO \rightarrow (CH_2)_6N_4 + 2H_2SO_4 + 6H_2O$$

The digest is neutralized and treated with formaldehyde and the resulting acid is titrated.

The use of sodium hypobromite (*35*) has been adapted to micro-Kjeldahl procedure particularly in the determination of nitrogen in milk This is a very satisfactory method for small amounts of nitrogen and is represented by the following reactions:

$$2NH_3 + 2NaOBr \rightarrow 2NaBr + N_2 + 3H_2O$$

$$NaOBr(excess) + 2KI + 2HCl \rightarrow 2KCl + NaCl + I_2 + H_2O$$

$$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI$$

The use of potassium biiodate (*3*) has also been suggested for small amounts of nitrogen. In the determination of nitrogen in petroleum feed stocks (*22*), a semimicro technique is used an aliquot of the distillate nesslerized, and the nitrogen estimated colorimetrically.

APPLICATION TO MORE COMPLICATED FORMS OF NITROGEN

In order to extend the scope of the Kjeldahl method to include a larger variety of nitrogen-containing compounds, numerous modifications have been suggested. The use of pure cotton cellulose as a reducing agent for some nitro and azo compounds was proposed by Bhat (*5*) for estimating the dyestuffs on fiber. Azo compounds can also be reduced by treatment with 50 to

100% powdered copper (*30*). Potassium iodide has been used frequently as a reducing agent. Rose and Ziliotto (*56*) applied this to the determination of nitrogen in nitriles. Preliminary reduction of nitrogen in side chains can be done by treatment with hydriodic acid and red phosphorus (*43*). Fish (*18*) reduced hydrazones, semicarbazones, and similar compounds by use of zinc dust and methanol in hydrochloric acid. It has been claimed (*63*) that by the use of mercury or mercury–selenium oxychloride catalysts, and prolonged digestion, refractory compounds such as pyridine, quinoline, and nicotinic acid can be determined. This procedure has been adapted to micro and semimicrodeterminations (*45*). Further work by Willits *et al.* (*70*) on refractory heterocycles showed that good results were obtainable with mercuric oxide, but that the results obtained by the addition of selenium were dependent upon the concentration of potassium sulfate and mercuric oxide, and digestion time. Perrin (*50*) found that the acid-salt-mercury ratio could be adjusted to the point where additional oxidizing agents were unnecessary. On the other hand, Dupuy (*17*) determined the nitrogen in pyridine by the use of selenium oxychloride, 40 grams of potassium sulfate, and 1-hour digestion time.

For nitro compounds, the use of salicylic acid is generally established, followed by reduction with sodium thiosulfate. As this involves two separate operations, McCutchan and Roth (*38*) suggested the use of thiosalicylic acid in place of salicylic acid and sodium thiosulfate, and the increase of potassium sulfate to 20 grams. Their results indicate a marked improvement and increase the scope of the method. Lake (*31*), in a report on cooperative work on nitrogen in petroleum and shale oil, also found that thiosalicylic acid gave results comparing favorably with the Dumas and ter Meulen methods.

Hydroxy compounds such as phenol and salicylic acid aid in the conversion of nitro groups and other nitrogen groupings. A study of various hydroxy compounds (*8*) showed that 1-naphthol–pyrogallol in combination with sodium thiosulfate and 18 grams of potassium sulfate gave a marked increase in the amount of nitrogen recovered from refractory compounds, and in some cases reached theoretical values.

The importance of a general method for all forms of nitrogen need not be emphasized. Fundamentally, the physical operation of the method is simple, and has a further advantage in that it can be run in multiple. Whether or not a single modification embracing all forms of nitrogen can be developed will be in the hands of those workers to whom the Kjeldahl method is a valuable tool.

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Determination of Total and Primary Hydroxyl in Cellulose Esters by Ultraviolet Absorption Methods

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Different amounts of primary and secondary hydroxyl groups are formed during the hydrolysis of cellulose acetate, depending on the exact conditions of hydrolysis. As the properties of the hydrolyzed cellulose ester depend on the relative amounts of the different hydroxyls, this information is desirable for characterizing the ester. Ultraviolet absorption measurements have been used to measure quantitatively the amounts of carbanilate and of trityl introduced into hydrolyzed cellulose acetate by reaction with phenyl isocyanate and trityl chloride, respectively. Measurement of the carbanilate content allows calculation of the total hydroxyl, and measurement of the trityl content allows calculation of the primary hydroxyl in the original material. These methods have been applied to a wide variety of cellulose esters, and their precisions have been evaluated using a typical sample of cellulose acetate.

A PRIOR method (*6*) for determining total hydroxyl in cellulose esters depends on acetylating the hydroxyl groups with acetic anhydride. The excess reagent is hydrolyzed and titrated to indicate the hydroxyl content. Since a liberal excess of reagent must be taken, this method depends on small differences between the relatively large titrations of blank and sample.

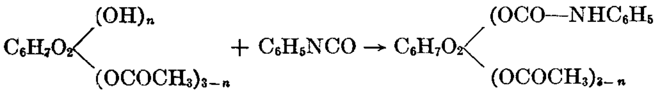
Phenyl isocyanate has been shown to react rapidly and completely with the hydroxyl groups in hydrolyzed cellulose acetate in pyridine solution at 100° C. to form a carbanilate (*N*-phenyl carbamate). The excess phenyl isocyanate may be removed by precipitating and washing the product in alcohol. The amount of carbanilate introduced can be quantitatively determined from the ultraviolet absorbance at 280 mμ.

Primary hydroxyl in cellulose esters has been determined by tosylation-iodination (*3, 7*) and by tritylation (*8*). The amount of trityl introduced has been determined (*5*) by dissolving the tritylated product in concentrated sulfuric acid and precipitating the triphenylcarbinol in water. In the present paper the amount of trityl is determined from the ultraviolet absorbance at 259 mμ.

TOTAL HYDROXYL BY CARBANILATION

The course of the reaction between cellulose acetate and phenyl isocyanate in pyridine at 100° C. was followed by quantitative recovery of product (see experimental section). The data in Table I indicate complete reaction after 1 hour or less, confirming the results of Hearon *et al.* (*4*). This is the method referred to as a new procedure in the interlaboratory study on the determination of acetyl (*9*), and the samples referred to in Table I are the same as used in that study.

The reaction of phenyl isocyanate with a partially hydrolyzed cellulose acetate may be represented by Equation 1.



$$C_6H_7O_2\begin{cases}(OH)_n \\ (OCOCH_3)_{3-n}\end{cases} + C_6H_5NCO \rightarrow C_6H_7O_2\begin{cases}(OCO\text{—}NHC_6H_5)_n \\ (OCOCH_3)_{3-n}\end{cases} \quad (1)$$

The per cent acetyl in the cellulose acetate is given by

$$\% \ Ac = \frac{43(3 - n)}{288 - 42n} \times 100 \quad (2)$$

and the per cent carbanilate, *c*, in the derivative is given by

$$c = \frac{119n}{288 - 42n + 119n} \times 100 \quad (3)$$

Combining Equations 2 and 3, eliminating *n*, gives the per cent acetyl of the original cellulose acetate in terms of the per cent carbanilate, *c*, in the derivative:

$$\% \ Ac = \frac{4480 - 65.1c}{100 - c} \quad (4)$$

Equation 4 is valid when acetyl is the only substituent in the starting material, and provided the degree of polymerization is not excessively low.

Table I. Time Series for Carbanilation of Cellulose Acetate

Sample	Reaction Time, Hours	Carbanilate, %	OH, %	Acetyl, % From carbanilate	Acetyl, % By saponification
1	0.5	16.40	2.81	40.8	40.53[a]
	1	17.33	3.00	40.55	40.42[b]
	2	17.38	3.01	40.5	...
	3	17.43	3.02	40.5	...
	4	17.70	3.07	40.45	...
2	0.5	22.12	4.06	39.0	39.05[a]
	1	22.43	4.13	38.9	38.97[b]
	2	22.13	4.06	39.0	...
	3	22.45	4.14	38.9	...
	4	22.16	4.07	39.0	...

[a] Interlaboratory study (*9*).
[b] Average values, this laboratory.

To calculate the per cent total hydroxyl from the per cent carbanilate in the derivative, the hydrolyzed cellulose ester may be considered as a simple alcohol:

$$R\text{—}OH + C_6H_5NCO \rightarrow C_6H_5NH\text{—}COOR \quad (5)$$

The per cent total hydroxyl in the starting material is given by

$$\% \text{ total OH} = \frac{17}{R + 17} \times 100 \quad (6)$$

and the per cent carbanilate, *c*, in the derivative is given by

$$c = \frac{119}{R + 136} \times 100 \quad (7)$$

Combining Equations 6 and 7, eliminating *R*, gives the per cent total hydroxyl in the original cellulose ester in terms of the per cent carbanilate in the derivative:

$$\% \text{ total OH} = \frac{14.3c}{100 - c} \quad (8)$$

Equation 8 is valid regardless of the nature of the acyl groups and the degree of polymerization.

The carbanilates absorb strongly in the ultraviolet where cellulose acetate is almost transparent. The spectrophotometric curves of cellulose acetate (sample 1, Table I) and the carbanilate and trityl ether derived from it are given in Figure 1. These curves were made on a Cary recording spectrophotometer, balanced out with air in both beams. The peak at 280 mμ was chosen for quantitative measurement. At this wave length, the absorbance of cell plus solvent was the same as when cellulose acetate was present. Quantitative measurements were made with a Beckman Model DU spectrophotometer balanced with cell and solvent.

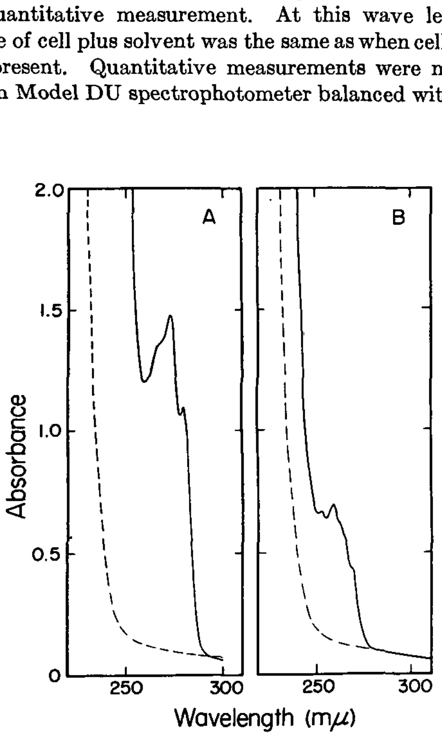


Figure 1. Spectrophotometric Curves of Cellulose Acetate and Its Carbanilate and Trityl Ether Derivatives

A. —— Cellulose acetate carbanilate
- - - - Cellulose acetate
B. —— Cellulose acetate trityl ether
- - - - Cellulose acetate

A series of ten samples with acetyl contents varying from 32 to 44% was carbanilated. The products were recovered quantitatively as "skin" precipitates by pouring alcohol into the reaction mixtures. Additional carbanilates were prepared from these ten samples, obtaining the products in the conventional flake form by pouring the reaction mixtures into alcohol. The absorbances of both sets of products were in close agreement. Figure 2 shows the relationship between the per cent carbanilate and absorbance at 280 mμ of a 0.1% solution of the cellulose acetate carbanilate in methylene chloride–methanol (90 to 10 by weight). The data are well represented by a straight line over this range. Thus the per cent carbanilate may be obtained by multiplying the absorbance by 17.1.

PRIMARY HYDROXYL BY TRITATION

The method of determining trityl content of cellulose acetate trityl ethers by dissolving the sample in concentrated sulfuric acid and precipitating the triphenylcarbinol by addition of water (*5*) has given generally satisfactory results. However, when the amount of trityl is low, the precipitated triphenylcarbinol does not coagulate readily and either clogs or passes through the filter.

The trityl group absorbs strongly in the ultraviolet. Figure 1,*B*, shows the spectrophotometric curve of the cellulose acetate trityl ether derived from sample 1, Table I. Gravimetric trityl determinations and ultraviolet absorbance readings at 259 mμ were made on a number of samples. The results are plotted in Figure 2. Cellulose acetate has an average absorbance of 0.015 under these conditions, and the absorbance of the trityl ether is corrected by this amount. The absorbance varies directly with the trityl content. The per cent trityl may be determined by multiplying by 25.3 the corrected absorbance of a 0.1% solution.

In deriving an equation to calculate per cent primary hydroxyl from per cent trityl, the reaction may be considered simply:

$$R\text{—OH} + Tr\text{Cl} = \text{C}_5\text{H}_5\text{N} \rightarrow R'\text{—O}Tr + \text{C}_5\text{H}_5\text{N.HCl} \quad (9)$$

where *Tr* represents triphenylmethyl (molecular weight 243) and *R'* represents all of the hydrolyzed cellulose acetate except the primary hydroxyl. The per cent primary hydroxyl in the starting material is given by

$$\% \text{ primary OH} = \frac{17}{R' + 17} \times 100 \quad (10)$$

and the per cent trityl, *t*, in the derivative is given by

$$t = \frac{243}{R' + 259} \times 100 \quad (11)$$

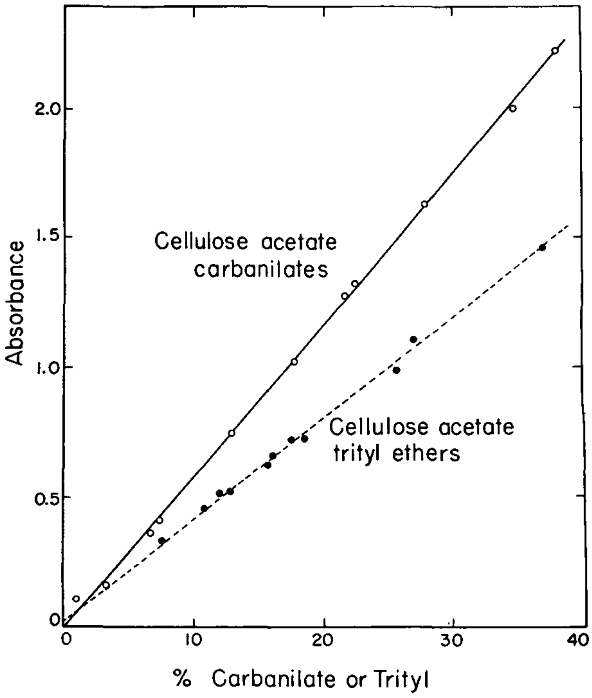


Figure 2. Per Cent Carbanilate or Trityl *vs.* Absorbance

0.1% solution of cellulose acetate carbanilate or cellulose acetate trityl ether in methylene chloride methanol (90–10 by weight)

Table II. Trityl Content of Cellulose Acetate Trityl Ethers

	Trityl, %			
	Flake Precipitate		Skin Precipitate	
Sample	Recovery of triphenylcarbinol	Ultraviolet absorbance	Recovery of cellulose acetate trityl ether	Ultraviolet absorbance
3	12.2	12.5	12.2	12.9
4	23.3	23.0	23.7	24.2
5	26.1	26.5	27.4	27.0

Combining Equations 10 and 11, eliminating *R'*, gives the per cent primary hydroxyl in the original cellulose acetate in terms of the per cent trityl in the derivative:

$$\% \text{ primary OH} = \frac{7.02t}{100.4 - t} \quad (12)$$

The quantitative recovery of product has also been used as a method for trityl determinations. Products obtained in this way are referred to in Table II as skin precipitates in contrast to the conventional flake precipitates. The data in Table II show the agreement among the methods for determining trityl content.

PRECISION AND RANGE OF THE METHODS

In a study of the precision of these methods, sample 1 of Table I was carbanilated and tritylated 32 times. The reactions were carried out in groups of two on different days, but the absorbances were measured at the same time (Table III). The mean total and primary hydroxyl contents were 3.026 and 1.134%, respectively. The standard deviations for a single value were 0.020 and 0.030%, respectively

Table III. Precision of Total and Primary Hydroxyl Determinations

Operator	Total OH, %		Primary OH, %	
A	3.01	3.01	1.19	1.16
	3.01	3.11	1.16	1.08
	3.03	3.03	1.17	1.17
	3.00	3.00	1.09	1.11
	3.04	3.04	1.16	1.09
B	3.05	3.09	1.14	1.16
	3.05	3.03	1.11	1.15
	3.04	3.03	1.16	1.15
	3.10	3.01	1.13	1.08
	3.03	3.02	1.11	1.11
C	3.00	3.02	1.11	1.16
	3.00	2.83[a]	1.14	1.12
	2.98	3.00	1.14	1.12
	3.00	3.01	1.12	1.13
	3.02	3.01	1.10	1.17
	3.01	3.02	1.07	1.14
Mean	3.026		1.134	
Average range of pairs	0.023		0.034	
Standard deviation of single value, based on average range of pairs	0.020		0.030	

[a] Value omitted, as duplicate solutions prepared from this sample all gave low and variable results.

Both methods have been applied to cellulose acetates containing 30 to 44.8% acetyl and to a wide variety of commercial cellulose acetate propionates and cellulose acetate butyrates.

Repeated absorbance measurements at different concentrations confirmed the earlier work of Ayres (*1*) that the useful range of absorbance of the Beckman Model DU spectrophotometer extends from about 0.2 to 1.6.

EXPERIMENTAL

Carbanilation with Quantitative Recovery of Product. A sample of approximately 0.5 gram of cellulose acetate was placed in a tared 125-ml. glass-stoppered Erlenmeyer flask and dried for 2 hours at 100° C. Reweighing after cooling gave the weight of starting material. The cellulose ester was dissolved by standing overnight in 5 ml. of anhydrous pyridine. Then 0.5 ml. of phenyl isocyanate was added, and the flask was placed in a 100° C. electric oven. After the contents of the flask had come to temperature, the phenyl isocyanate was mixed in by tilting the flask from side to side several times. After 2 hours' reaction time, the flask, with the stopper slightly ajar, was cooled intermittently with tap water. During the cooling period the solution was distributed over the interior by rotating and tilting the flask to a pouring position. Care was taken to prevent the solution from coming in contact with the ground-glass stopper. The thoroughly chilled solution was so viscous that it flowed very slowly to the bottom of the flask. The product was precipitated by quickly filling the flask with 95% ethyl alcohol. Ideal precipitates remained transparent for several minutes and gradually became white and opaque. After half an hour the precipitate could be stripped in practically one piece from the interior of the flask using a narrow spatula. The supernatant liquid was decanted through a tared 60-ml. sintered-glass funnel of coarse porosity (Corning No. 36060). The precipitate was washed with four changes of alcohol, each of at least half-hour duration. On the last wash the precipitate was transferred quantitatively to the funnel. After allowing most of the alcohol to evaporate at room temperature, the precipitate was dried overnight at 100° C. and weighed.

Carbanilation for Ultraviolet Absorbance. A sample of approximately 0.5 gram of cellulose acetate was placed in a 15-ml. screw-cap bottle and dried at 100° C. for 2 hours. After dissolving the ester in 5 ml. of anhydrous pyridine, approximately 0.5 ml. of phenyl isocyanate was added and thoroughly mixed in with a small stirring rod. For samples whose anticipated acetyl content was below 39%, the amount of phenyl isocyanate was increased by 0.1 ml. for each 2% acetyl below that amount. After 2 hours of reaction at 100° C., the solution was diluted with 2 to 10 ml. of pyridine, depending on the viscosity, and the product was precipitated by pouring, with stirring, into 95% alcohol. The precipitate was filtered on a small Büchner funnel and transferred to a 4-ounce screw-cap bottle. Two half-hour washes on the shaker were sufficient to remove all the excess reagent. After drying at 100° C., a sample of 0.1231 gram was dissolved in 100 ml. (123.1 grams) of methylene chloride–methanol (90 to 10 by weight). The absorbance was measured at 280 mμ on a Beckman Model DU spectrophotometer (Serial Number 61361).

Carbanilation of Highly Esterified Cellulose Acetate. A reaction container was constructed from a pair of 24/40 standard-taper (borosilicate) ground-glass joints. A test tube, approximately 20 × 150 mm., was fashioned from the outer part of the joint by closing the open end in a blast lamp. The inner part was drawn to a constriction just above the ground glass and a short length of 6-mm. tubing was sealed on. The stirrer consisted of a length of 4-mm. glass rod bent at a right angle of the bottom in the form of a semicircle. The stirring shaft had sufficient cooling capacity to prevent loss of pyridine when heated in an oil bath at 115° to 120° C. A reaction period of 30 minutes with occasional stirring was found to be sufficient. By shortening the drying period of the starting material to 30 minutes and of the carbanilated product to 1 hour at 110° C., the elapsed time can be reduced—if necessary to about 6 hours. This method was applied to a highly acetylated cellulose acetate of the type currently used for motion picture film (*2*). Four determinations in parallel on a typical sample gave hydroxyl contents corresponding to 43.54, 43.52, 43.55, and 43.54% acetyl, respectively.

Tritylation of Cellulose Acetate. The determinations based on quantitative recovery of product were made in a manner similar to the carbanilations. A sample of 0.5 gram was dissolved in 2.5 ml. of pyridine in a 125-ml. flask and allowed to react with 0.5 gram of trityl chloride for 24 hours. At the end of the reaction the solution was diluted with a sufficient pyridine to give a good precipitate.

In the preparation of trityl derivatives for ultraviolet absorbance, 1 gram of cellulose ester was dissolved in 5 ml. of pyridine in a 15-ml. bottle and allowed to react with 1 gram of trityl chloride. For samples having more than 0.50 hydroxyl per glucose unit, the amount of trityl chloride was increased according to the formula previously given (8).

ACKNOWLEDGMENT

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Use of Infrared Radiation for Detection of Colorless Substances on Paper Chromatograms

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It is desirable to have a general physical method for detecting colorless substances on paper chromatograms. For this purpose an apparatus has been developed to record infrared emission and transmission properties of paper strips. It has been found possible to detect a variety of substances in milligram quantities without the aid of a spectrophotometer.

ONE of the important problems in the field of paper chromatography is the development of general techniques for detecting small amounts of colorless substances upon the completed chromatogram. The incorporation of radioisotopes into the substances to be separated resolves the problem of detection into that of locating the radioactive zones on the completed chromatogram for which several methods are available (*6, 10, 14*). Absorption of ultraviolet radiation has also been used to locate colorless zones either by the fluorescence imparted (*2, 3, 12*) or by direct transmission measurements of the completed chromatograms (*4, 11, 16*). Still, the paper chromatographic methods are largely limited to the separation of colored compounds or those which can be converted to colored compounds by means of some chemical reaction on the paper.

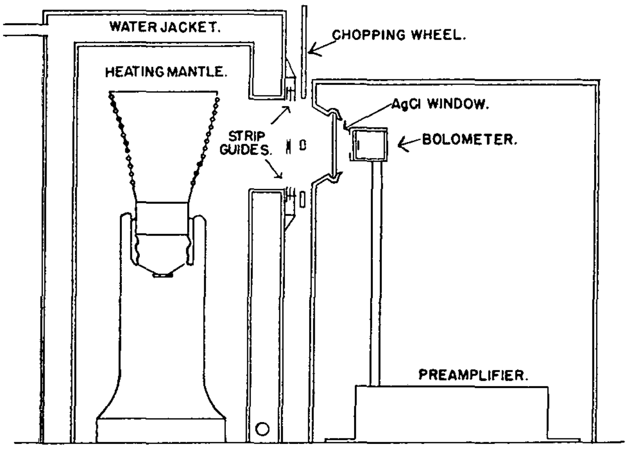

Figure 1. Schematic Diagram of Apparatus

Center section

The ability of infrared radiation to interact with practically all types of matter suggested that it could be utilized in an extremely general method for locating substances which were not visible in ordinary light. In addition, its great specificity of interaction suggested the possibility of not only finding the separated zones but also distinguishing the chemical composition of one from another. Although spectrophotometry would be most advantageous in dealing with the question of specificity, there is also the possibility of using a negative or positive filter technique as used in infrared gas analyzers (*5, 7, 9*).

GENERAL METHOD

The general plan was to compare the emission or transmission of infrared radiation by a developed paper chroamtogram with the same properties of plain filter paper. The instrument developed for this purpose is shown in Figure 1. The developed chromatogram in the form of a narrow paper strip 2 × 30 cm. and a similar strip of plain filter paper which had been cut successively from the same sheet of paper could be mounted in the two steel guides placed in front of an electric heating mantle. Each strip could be pulled through the guide at a constant rate by a small motor, as shown in Figure 2. Along each guide are two concentric rectangular apertures, 0.50 × 1.60 cm., one in each wall. As a section of paper strip passes between these apertures, it is exposed on one side to the heating mantle, and radiation transmitted or emitted by the paper is allowed to pass out the aperture on the other side toward the detector.

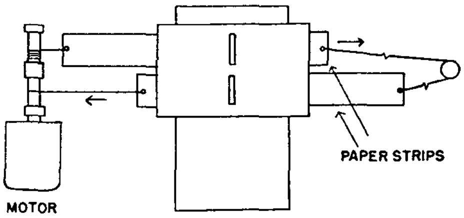

Figure 2. Schematic Diagram of Apparatus

As seen from bolometer housing

A motor-driven chopping wheel was interposed between the guides and the detector in such a manner that radiation was allowed to pass through from alternately one and then the other paper strip at a rate of 20 cycles per second. This pulsating radiation beam then had an intensity amplitude equal to the difference in the intensities of radiation coming from the two paper strips. The detector consisted of a thermistor-type bolometer enclosed in a metal jacket and fitted with a rock salt window. The bolometer and preamplifier were further enclosed in a metal housing fitted with a silver chloride window coated with silver sulfide to exclude visible radiation. The alternating intensity of the radiation striking the active thermistor flake gave rise to an alternating electric signal which was then amplified, rectified, and recorded.

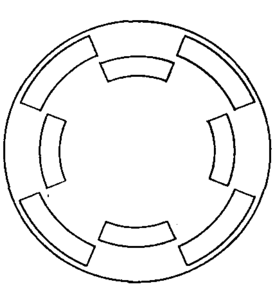

Figure 3. Chopping Wheel

INSTRUMENTAL DETAILS

The heating mantle used was a commercial Nichrome wire heater mounted on a ceramic base and operated through a Variac. The chopping wheel is shown in Figure 3 and was constructed out of a $^1/_{16}$-inch sheet aluminum and rotated at a speed of 300 r.p.m. by a small motor. The surface facing the bolometer was polished to a mirror finish in order to lower its emissivity. The radiation detector used was a thermistor bolometer, Type BG-1, which, together with the preamplifier, was manufactured by the Servo Corp. of America. Operating at a bias voltage of 150 volts and a radiation interruption rate of 20 cycles per

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second, the detector should have a sensitivity of approximately 470 volts per watt. After passing through the preamplifier with a listed gain of 330, the signal was sent to a Type 1231A amplifier-null detector manufactured by the General Radio Co. The null detector circuit rectified the alternate current signal and operated a direct current milliammeter which acted as a null detector. An Esterline-Angus recording milliammeter, Type AW, was placed in series with the null meter and was run at a chart speed of 2 scale divisions (1.5 inches) per minute. The combination amplifier–null detector–recorder was calibrated with a standardized 20-cycle-per-second test signal over the range of both amplifier gain settings and null point settings since the null meter scale is logarithmic.

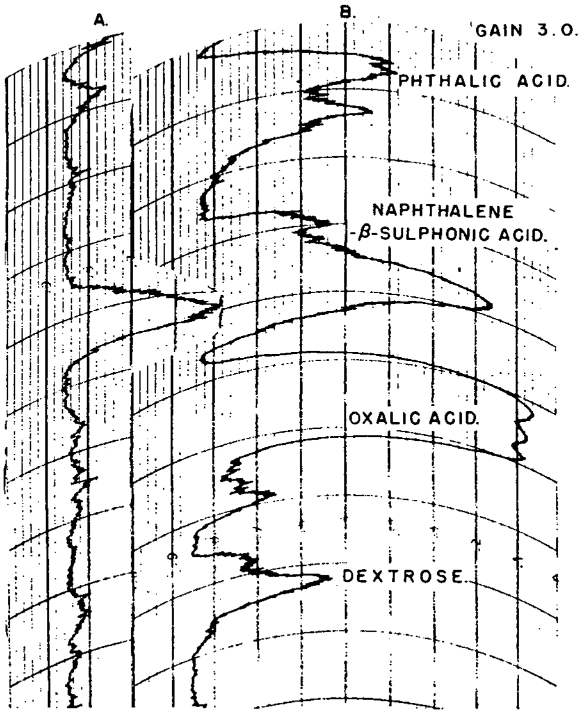

Figure 4. Comparison of Paper Chromatograms

A. Comparison of two blank paper strips
B. Comparison of same dry strip after samples were applied

The noise level of the apparatus viewed at the output of the preamplifier was found to be approximately 5 mv. (root mean square). Using the listed sensitivities for the bolometer and preamplifier, the minimum detectable power by the apparatus can be estimated to be about 3×10^{-8} watt.

A recorded signal of zero could be obtained when sections of plain filter paper were being viewed in both guides by adjusting either the width of the apertures in front of the paper strips or the null point scale setting. Differences in emission or transmission of other sections of a developed chromatogram would then be recorded as deviations from this null point.

As a means for estimating the temperature of the strip as it passed into the radiation beam, various types of wax were rubbed on the paper surface toward the source. As a section of paper containing a wax having a melting point lower than the temperature acquired by the paper in the radiation beam, the wax would melt, changing the translucence of the strip markedly. By adjusting the water temperature in the source housing and the voltage at the heating mantle, the temperature of the strip was kept between 50° and 60° C. when the strips were pulled through at the normal rate of 1 inch per minute.

EXPERIMENTAL

The paper used throughout the investigation was Whatman No. 1 filter paper. The transmission of this paper versus air, as measured with a Beckman Model IR-2 spectrophotometer, was found to vary from 0.2 to 0.3% in the wave-length range of 1 to 10 microns, much of the radiation, of course, being scattered. Strips of this paper were prepared with samples of various colorless compounds deposited upon them. These compounds included citric acid, dextrose, malic acid, maltose, naphthalene-2-sulfonic acid, oxalic acid, phthalic acid, potassium chloride, succinic acid, sulfanilamide, tartaric acid, and urea. They were applied as solutions and after they had dried a sample strip and its reference strip of plain filter paper were placed in the strip guides and compared. All of the substances investigated were easily detectable when 8 mg. of sample were between the apertures. For several compounds it was of interest to find the limiting amount which could be detected using this method of comparing dry paper strips. In the case of oxalic acid, amounts as little as 0.5 to 0.7 mg. uniformly spread over the total area of the aperture could consistently be detected. On the other hand, the detection limit for dextrose was approximately five times higher.

A typical recording of a prepared strip is shown in Figure 4, *B*. Figure 4, *A*, shows a recording from the same regions viewed in Figure 4, *B*, before the samples were applied, showing that the instrument is also capable of detecting differences in plain paper strips, even though they be cut successively from the same sheet of paper. Attempts to eliminate such nonuniformities of the paper by washing were unsuccessful; however, they may be due to simply a varying thickness of the paper strip. Recordings of this type are reproducible to the extent shown in Figure 5, provided the same regions of each strip are matched against each other during the runs. This can be done at the beginning of a series by marking a line on each paper strip at the place where it emerges from the guide. The strips can then be reset to these positions at the beginning of the successive run.

The instrument measures only the magnitude of the difference in intensities of radiation coming through the apertures in front of the sample and standard strips. A supplementary technique must be used to determine which radiation beam is more intense. A change in the size of the aperture in front of the reference strip gives this information conveniently. All the compounds listed caused a decrease in the intensity of radiation.

Another technique tried in order to detect substances on filter paper was to apply heavy mineral oil to the paper strips after the

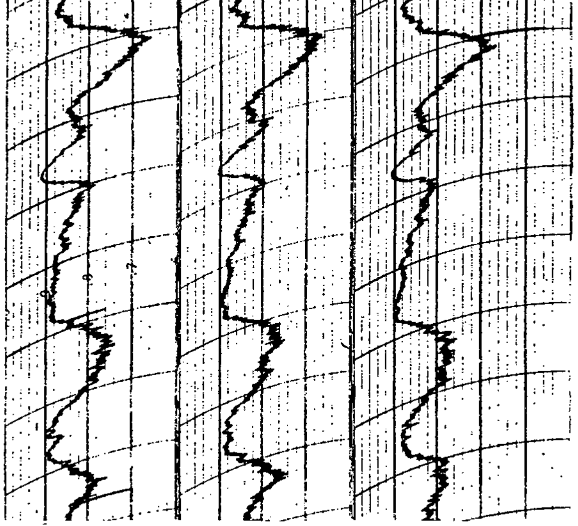

Figure 5. Duplicates of Dry Strip Comparisons

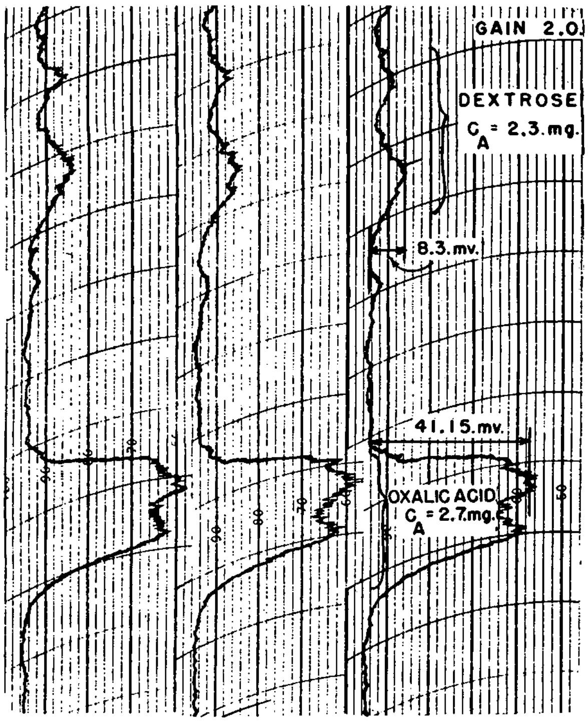

Figure 6. Recordings of Developed Chromatogram Containing Oxalic Acid and Dextrose

C_A is maximum amount of a material between the apertures at any instant

samples had been deposited. The oil was painted on the paper with a soft camel's-hair brush and any excess which remained on the surface was blotted off until no oily gloss remained. The transmission of the paper in this condition as measured with a Beckman Model IR-2 spectrophotometer had risen at some wave lengths in the range 1 to 10 microns to as high as three times the transmission of the unoiled paper. Apparently at these wave lengths, a decrease in the radiation reflected from the surface had more than offset any increase in radiation absorbed by the paper due to the oil present. Strips of oiled paper containing samples distributed at various spots were compared with plain oiled paper in the same manner and conditions used with the unoiled paper strips. As in the previous technique, the presence of any of the compounds listed caused a decrease in the intensity of the radiation. Recordings of these comparisons were found to be very reproducible, and reoiling of the paper had little effect on the chart obtained. In general, this method was much more sensitive, an oxalic acid sample giving six times as great a response by this method as in the comparison of dry strips.

Using either of the described techniques, the deflections obtained for oxalic acid, evaluated in terms of millivolts, were not found to follow a linear relationship with respect to amount. From the data available it was not possible to decide whether this behavior was a property of the system measured or whether the fault lay with the manner in which the deflections were evaluated.

APPLICATION TO DEVELOPED CHROMATOGRAMS

Operating the apparatus under the conditions described in the previous section, developed chromatograms were examined by both the comparison of dry strips and oiled strips. One of the systems separated and detected was a mixture of oxalic acid and dextrose. A sample of a solution containing approximately equal quantities of these two substances was applied 2 inches from one end of a strip of filter paper. After drying, the strip was suspended in an enclosed glass cylinder with the end nearest the sample immersed about 1 cm. in a reservoir of *n*-butyl alcohol saturated with water. In approximately 4 hours, the chromatogram was sufficiently developed so that the bands of oxalic acid and dextrose were clearly separated.

The bands could be detected either by using the apparatus or by painting a solution of bromothymol blue in the area suspected of containing the oxalic acid and a solution of ammoniacal silver nitrate in the region suspected of containing the dextrose. Using the oil technique, Figure 6 shows the recordings of such a separation and the reproducibility attainable.

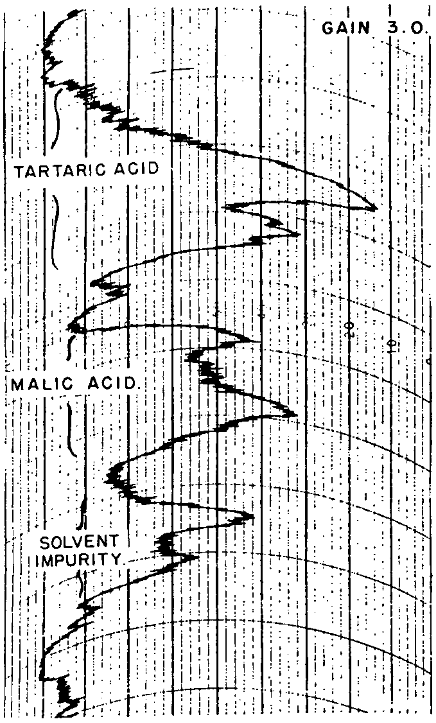

Figure 7. Recording of Developed Chromatogram Containing Malic and Tartaric Acids

Chromatograms of oxalic acid and dextrose were also examined by comparing dry strips of filter paper; however, the procedure required was more tedious. First, two plain strips of filter paper cut successively from the same sheet of paper were compared in the apparatus. A sample of the mixture was then applied to one of the strips and it was developed as described previously. The developing solvent was also allowed to rise in the other strip in case the solvent would have any effect on the paper. After drying, the strips were again compared at the same gain setting on the amplifier. The solvent appears to have had very little effect on the strips, since the deflections which showed up in the comparison of the plain strips also showed up in the comparison of the developed strips.

Another system which was investigated was that of a mixture of tartaric and malic acids. The procedure used for separation was the same as that described previously, except that the developing solvent consisted of *n*-butyl alcohol saturated with an aqueous solution of 1*N* acetic acid (*8*). After development, the strip was placed in a drying oven at 60° C. to remove any acetic acid, and then compared with its reference strip of plain paper in the apparatus using the oil technique. Figure 7 shows a recording of such a chromatogram. In this case, a third component appeared in the developed chromatogram right at the solvent front. This material was yellow in color and was due presumably to some impurity in the *n*-butyl alcohol used in this case.

USE OF NEGATIVE FILTER

In order to test the possibilities of identifying the separated components on a chromatogram, a negative filter was prepared for use in the identification of the components of the dextrose–oxalic acid separation. A saturated solution of oxalic acid in ether was added to a stock solution of collodion and a sample of this mixture was placed on a glass plate and allowed to dry. The film thus formed was 0.0025 inch thick and was found to contain 30% oxalic acid by weight. When examined with a spectrophotometer, the film was found to have the absorbance spectrum versus air shown in Figure 8, *A*.

To examine the extent to which this film is characteristic of the oxalic acid it would be desirable for comparison to have an exactly similar film with the oxalic acid removed. Difficulties in standardizing the preparation of such films, and, in particular, the uncertainty as to what the oxalic acid film would be like if the oxalic acid were removed, prevented this direct comparison. The absorbance spectrum of a plain collodion film is shown in Figure 8, *B*, in order to gain some idea of what the oxalic acid film would transmit if the oxalic acid were not there. Considering the thickness of the films and their densities, it is felt that approximately equal amounts of material are compared in these two spectra; however, in the case of the oxalic acid film, only two thirds of the material is collodion. It would thus seem that the absorbance of the collodion portion of the oxalic acid film would be, in general, about two thirds of the values shown for the plain collodion film in Figure 8, *B*.

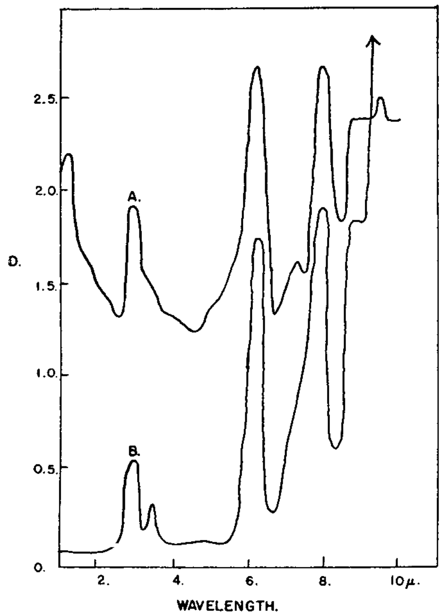

Figure 8 Infrared Absorption Spectra

A. Oxalic acid filter
B. Collodion film

Although similar, these spectra show decided differences between 1 and 2.5 microns and again between 4.5 and 6.0 microns. Spectra of collodion (*15*) and oxalic acid crystals (*13*) found in the literature show that oxalic acid has a broad absorption band between 5 and 6 microns with sharp bands at 2.8, 7.4, and 8.0 microns, while collodion has sharp bands at 3.0, 7.1, and 8.0 microns. The absorption spectrum of dextrose crystals has been published only for the range 1.6 to 4.6 microns (*1*). These data were felt to be insufficient to predict whether the filter prepared would actually act selectively as a negative filter; however, it was felt that the structural differences between oxalic acid and dextrose might be great enough so that some effect might be observed with even such a crude filter.

This guess appears to be correct as shown in Figure 9. Chart *B* corresponds to the comparison of a developed chromatogram of oxalic acid and dextrose with its reference strip of plain paper, using the oil technique. Chart *A* corresponds to the comparison of the same strips after interposing the oxalic acid film in front of both apertures. The film was mounted in a cardboard frame and was placed in a prepared holder on the strip guide assembly so that it was between the paper strip and the chopping wheel.

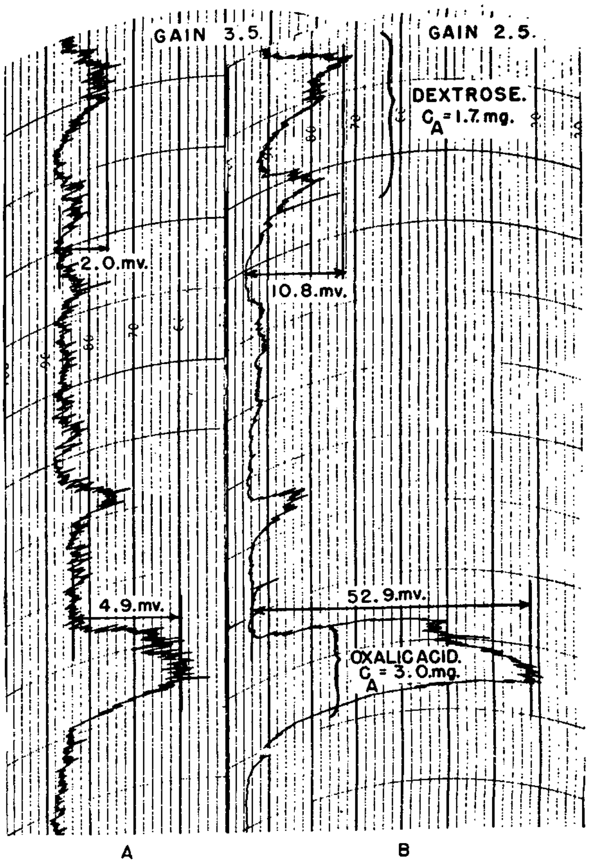

Figure 9. Recordings of Developed Chromatogram Containing Oxalic Acid and Dextrose

A. Before interposing filter
B. After interposing filter

The film attenuated the signal strongly so that the gain used for chart *A* was raised till the deflection given in the dextrose region was approximately the same as that shown in chart *B*. The deflection measured in millivolts given in the oxalic acid region is found to be attenuated to a much greater extent and shows a relative decrease of 91%, whereas the deflection decrease in the dextrose region is found to be 81%.

This effect can be interpreted in two ways. First, if transmitted radiation is being measured the film acts in the following way: Radiation characteristic of oxalic acid is absorbed from the radiation beam of the heating mantle by the oxalic acid on one paper strip. However, radiation characteristic of oxalic acid is being absorbed in both beams by the film so that the difference in intensities should be less than if the film were absent. On the other hand, radiation characteristic of dextrose will be absorbed by that substance on the sample strip, but the film will not absorb this radiation to as large an extent as it did radiation characteristic of oxalic acid. The signal from the dextrose region should then be less than it was without the filter, since all things absorb somewhat at all wave lengths, but the signal decrease should be proportionately smaller than the decrease of the oxalic acid signal.

This effect can also be interpreted in terms of selective emission from the oxalic acid on the paper strip followed by selective absorption by the film. Radiation characteristic of oxalic acid is emitted from that region on the paper strip and is selectively absorbed by the film. Also, however, radiation at these characteristic wave lengths is absorbed by the film in front of the plain paper strip, so that the signal from the oxalic acid region should be less than in the absence of the film. By a similar argument, the signal from the dextrose region would not be affected to such an extent.

DISCUSSION

The procedures described in the previous section have been shown to be capable of detecting a large assortment of chemical compounds and to be of some use in detecting the separated components on paper chromatograms. In the procedure involving the comparison of dry paper strips, the measured signal indicating the presence of a sample on the strip appears to be due largely to the lower temperature of the surface containing the sample. A sizable contribution to the signal, however, is due to either a decrease in the transmission of the paper in the sample region or a lowering of the emissivity of the surface containing the sample. No good method was found to distinguish between these latter possibilities. The relative insensitivity of the procedure in detecting sugars such as dextrose and maltose suggests that the chemical similarity of these substances with cellulose may give rise to similarities in the infrared emission and transmission of these substances.

The measured signal in the comparison of oiled paper strips appears to be almost entirely due to the transmission of radiation from the heating mantle. Heat capacity effects were shown to be small and there is no reason to expect that the large increase in signal after application of the oil is due to larger differences in emissivities. This procedure is also relatively insensitive to sugars, again suggesting the influence of similarity in chemical structure between the sugars and cellulose. The greater sensitivity of this procedure together with the greater selectivity of transmission measurements over heat capacity measurements in identifying chemical compounds make this the preferred method.

Chromatographic separations on paper usually involve material quantities in the order of several micrograms, whereas the quantities which can be successfully detected by this method are in the order of several milligrams. Now, as has been shown, chromatographic separations can be made with such large amounts on filter paper, but the relative movement of the bands must be widely different. The major usefulness of paper chromatography on the other hand is its ability to deal with small samples and the trend of development for this technique appears to be in continually decreasing the sample size as soon as suitable detection methods become available. Thus, the present apparatus and technique cannot be considered as suitable for the detection of the majority of paper chromatograms.

By changing the arrangement of the apparatus so that the conditions for making transmission measurements are at an optimum, the detection limits of this technique might be extended down into a more useful range. Improvement in transmission measurements could be accomplished by increasing the infrared intensity emitted by the source after properly shielding the strips in some thermostated enclosure. It is possible that the application of other inert nonvolatile liquids to the strips would also improve their transmission properties. Because of the proximity of the noise level, a narrow band pass filter in the amplifier circuit would also be very desirable.

Some indication has been shown that transmittance measurements coupled with the use of a negative filter can be used not only to detect a substance but also to identify it. Here again, however, more quantitative work would be necessary to establish this technique firmly.

ACKNOWLEDGMENT

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Spectrophotometric Titrations with Ethylenediaminetetraacetic Acid(II)

Determination of Magnesium, Calcium, Zinc, Cadmium, Titanium, and Zirconium

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WIDE use of ethylenediaminetetraacetic acid or its sodium salts (EDTA, Versenate, Sequestrene, or Complexone III) as a volumetric agent has been possible because of the broad chelating power and stability of the Versenate chelates. Versenate forms a 1 to 1 chelate with a large number of di-, tri-, and, in some cases, tetravalent cations. By the proper use of buffers and additional complexing agents, the chelating power of the Versenate can be made very selective. This has been illustrated by Kinnunen and Merikanto in their procedure for the determination of zinc in the presence of copper by the addition of cyanide to an ammonia–ammonium chloride solution of the metals, using Erichrome Black T as an indicator (*2*). Cheng *et al.* have been able to determine calcium, magnesium, and iron in limestone with Versenate by varying the buffer conditions (*1*).

The over-all versatility, sensitivity, and general convenience of Versenate as a volumetric reagent are, however, dependent upon the means of end-point detection used for the various titrations. Pribil has described a potentiometric and amperometric procedure for the determination of several cations (*3*, *4*). The use of a spectrophotometric end point for the determination of iron(III), copper(II), and nickel(II) with Versenate has been described (*6*).

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In an effort to extend the versatility of ethylenediaminetetraacetic acid (Versenate) as a volumetric reagent, the ultraviolet region of the spectrum has been studied for use in the spectrophotometric determination of the end point of Versenate titrations. A procedure is given for the use of the spectrophotometric end point in the determination of the combined content of calcium, magnesium, cadmium, and zinc or for any one of these metals when present singly in ammonia–ammonium chloride buffered solutions; calcium in the presence of magnesium; and cadmium in the presence of zinc in sodium hydroxide solutions. A method for the determination of zirconium involves the titration of an excess of Versenate with iron(III) solution. A titanium-peroxide-Versenate complex was also found that was stable at low pH levels. The sensitivity of the spectrophotometric end point allows the use of Versenate solutions as dilute as 0.001*M* or less, even when the total volume of the solution being titrated is 100 ml.

In an effort to extend the use of the spectrophotometric end point in Versenate titrations, the ultraviolet region of the spectrum has been studied. A procedure is described for the determination of calcium, magnesium, cadmium, and zinc in ammonia–ammonium chloride solutions; calcium in the presence of magnesium; and cadmium in the presence of zinc. In addition, a volumetric method has been developed for the determination of zirconium, in which an excess of Versenate is added to a zirconium solution and the excess Versenate titrated with standard iron(III) solution using a spectrophotometric end point of the iron(III)–salicylic acid system.

The spectrophotometric end point is not only more versatile than the use of indicators in Versenate titrations but is also more sensitive. Versenate solutions as dilute as 0.001*M* will give a very sharp end point even when the total volume of the solution being titrated exceeds 100 ml.

A preliminary investigation of the nature of the titanium-Versenate and titanium–hydrogen peroxide–Versenate complexes was made. The use of either of these complexes for analytical purposes does not offer any decided advantages over existing methods for determining titanium.

APPARATUS

A Beckman model DU spectrophotometer was used for all the titrations with Versenate. The only modifications required for this instrument was the usual Beckman 10-cm. cell compartment, a quartz titration cell, and a cover for the cell compartment. The T-shaped titration cell, with a 7-cm. light path, was similar in every respect to the cell described previously (*6*) except that the cell was made from quartz. This quartz cell allowed titrations to be made at wave lengths as low as 215 mμ. A Bakelite cover was made to fit over the 10-cm. cell compartment of the spectrophotometer. In the center of this cover, a 3.5-cm. hole was made which allowed the lower portion of the titration cell to rest on the base of the cell compartment while the neck of the cell protruded above the cover. The motor-driven stirrer and 10-ml. microburet were the same as previously described (*6*).

REAGENTS

Standard Versenate, 0.0134*M*. Approximately 5.0 grams of disodium dihydrogen ethylenediamine tetraacetate dihydrate were dissolved in water and diluted to 1 liter. This solution was then standardized against the standard calcium solution using the spectrophotometric end point.

Standard Versenate, 0.0013*M*. Twenty-five milliliters of the 0.01338*M* Versenate were diluted to 250 ml. with redistilled water, and the molarity was checked against standard calcium solution. The molarity found by this procedure was 0.001321, indicating that very dilute Versenate solutions should not be prepared by dilution from an aliquot of standard Versenate without further standardization.

Standard Calcium, 0.01*M*. An accurately weighed amount of reagent grade calcium carbonate (1.0 gram) was dissolved in hydrochloric acid and the resulting solution diluted to 1 liter.

Standard Zirconium, 1.035 mg. per ml. Ignited zirconium dioxide (99.9% purity) was dissolved by a potassium bisulfate fusion. The final solution was 3.6*N* in hydrochloric acid.

Standard Titanium, 1.043 mg. per ml. Ignited pure titanium dioxide was taken into solution by a potassium bisulfate fusion. The final solution was 3.8*N* in hydrochloric acid.

Standard Magnesium, Cadmium, and Zinc, 0.01*M*. Solutions of these metals were prepared by dissolving accurately weighed quantities of the pure metals in hydrochloric acid and diluting the first solution to 1 liter.

Standard Iron(III), 0.018*M*. Reagent ferric ammonium sulfate was dissolved in water to which a few drops of sulfuric acid was added. The resulting solution was standardized against the Versenate solution.

Buffer Solution, pH 10. Sixty grams of ammonium chloride were dissolved in water to which were added 570 ml. of concentrated ammonia, and the solution was diluted to 1 liter with water.

SPECTROPHOTOMETRIC DETERMINATION OF END POINT

Spectra of Versenate and of magnesium Versenate, both at a pH of 10, are given in Figure 1. The spectra of zinc, cadmium, and calcium Versenate are similar to that of the magnesium chelate.

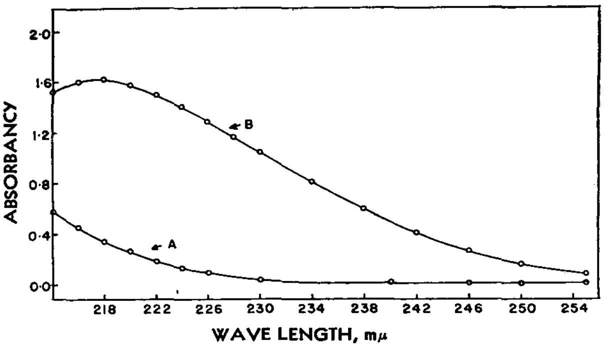

Figure 1. Absorption Spectra of Versenate and Magnesium Versenate

A. 1.33 × 10^{-3} Magnesium Versenate, pH 10
B. 1.33 × 10^{-3} Disodium Versenate, pH 10

The spectrum of the Versenate at pH 10 is due to the HY^{---} and Y^{----} anions of the Versenate. A similar spectrum is exhibited by Versenate solutions from a pH of about 7 to very alkaline media. At pH levels lower than 6.0, Versenate solutions show absorption spectra similar to that of the magnesium Versenate (curve *A* in Figure 1). It is possible, therefore, to make use of the large absorbancy exhibited by these anions of Versenate to determine end points spectrophotometrically in the titrations of several cations in alkaline solution with Versenate. Since the cations of magnesium, calcium, cadmium, zinc, and their Versenate chelates show little absorbancy at wave lengths above 222 mμ, the end point in the Versenate titration will be indicated by a sudden increase in the absorbancy of the solution caused by an excess of the HY^{---} or Y^{----} Versenate anions.

A typical titration curve for the titration of 83γ of magnesium with 0.0013*M* Versenate at a wave length of 222 mμ (magnesium concentration was 0.83 p.p.m.) is given in Figure 2. In titrations with 0.01*M* Versenate, a wave length of 228 mμ was employed when the pH 10 buffer was used. Although this is not the absorption maximum of the Versenate, the sensitivity is great enough at this wave length to give very sharp titration curves. In the Versenate titrations in more alkaline solutions and in alkaline citrate and cyanide solutions, the large absorbance of these reagents would not allow the adjustment of the spectrophotometer to zero absorbancy at the usual 228 mμ, so that wave lengths as high as 236 mμ were used when necessary. These wave lengths still gave very satisfactory titration curves.

In titrations of cations at pH levels much lower than 7, it is no longer possible to use the HY^{---} or Y^{----} absorption, so that other conditions must be found. In some cases it is possible to follow the course of the titration at a wave length where the metal Versenate shows a different absorbancy from the free metal ion and from the excess Versenate. An example of this type of titration curve is the manganese(II)–Versenate titration. At a wave length of 241 mμ and at a pH of 5.6 the manganese(II)–Versenate shows a stronger absorption than the free manganese(II) ions or the free Versenate. No further study was made of this system although the graph of absorbancy *vs.* milliliters of Versenate was a straight line and could undoubtedly be employed for the titration of manganese(II) solutions with Versenate.

A further spectrophotometric end-point procedure may be used for cations that show no spectral change when chelated with Versenate. This method would involve the addition of excess Versenate to the cation solution under question and then back-titration of the excess Versenate with another cation that will give a sharp end point while still not displacing the original metal Versenate chelate. This method has been used by Přibil for the determination of aluminum, copper, cadmium, zinc, nickel, and lead by titration of the excess Versenate with iron(III) and use of a potentiometric end point (*3*).

Similar titrations using the spectrophotometric end point of the iron(III)-salicylic acid system (*6*) should be possible, and would have the advantage that the exact end point would not have to be determined directly. This is a decided advantage in many titrations of this nature, since there is often a tendency for a slow equilibrium in the region of the end point.

The volumetric determination of zirconium by a back-titration of the excess Versenate with standard iron(III) solutions is possible by this spectrophotometric method. This back-titration is as fast and convenient as a direct titration and gives a very sensitive end point.

PROCEDURES

Standardization of Versenate. In the standardization of the Versenate solution with calcium, a 5- or 10-ml. aliquot of the standard calcium solution is pipetted into the titration cell, 2 ml. of pH 10 buffer is added, and the solution is diluted to 90 to 100 ml. with water. The wave length used for the titrations with 0.013*M* Versenate is 228 mμ; for more dilute Versenate solutions—i.e., 0.001*M*—a wave length of 222 mμ is employed. With the spectrophotometer set at the proper wave length, the usual spectrophotometric end point procedure (*5, 6*) is then used in the titrations of the calcium solution with the Versenate.

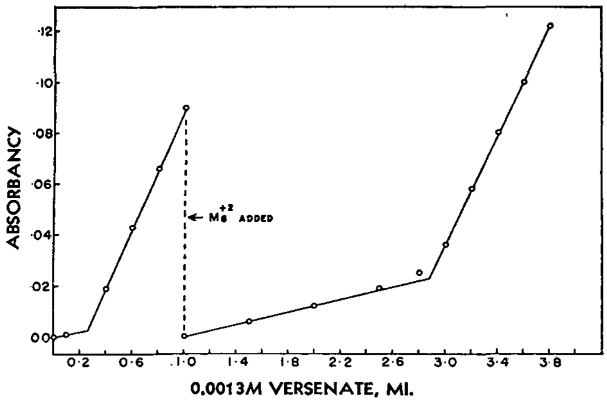

Figure 2. Titration of Magnesium with Standard Versenate

Wave length, 222 mμ; reagent blank given by first end point

When titrations are carried out with dilute Versenate solutions a blank should be run on the buffer and distilled water. Even with the 0.013*M* Versenate, this blank is sometimes of the order of 0.01 ml. or more so that it is advisable to check this blank periodically.

Determination of Calcium, Magnesium, Cadmium, and Zinc. The procedure for the titration of these cations is the same as for the standardization of Versenate with calcium.

Determination of Calcium in the Presence of Magnesium. Five milliliters of a citric acid solution (0.065 gram of citric acid per ml.) and 10 ml. of 6*N* sodium hydroxide are added to the titration cell with enough water to make a total volume of about 90 ml. The wave length of the spectrophotometer is set at 234 mμ and the solution titrated with the standard 0.013*M* Versenate, using the usual spectrophotometric end-point procedure. The end point in this procedure will give the amount of blank correction for the impurities present in the reagents.

After the end point has been passed and recorded, as indicated by the absorbancy of the solution, the calcium and magnesium solution is added to the titration cell and the Versenate titration continued until the second end point is reached. The amount of calcium is equivalent to the difference between these two end points. When several determinations of calcium are going to be made it is not necessary to determine the blank correction for every titration, provided the sodium hydroxide and citric acid are carefully measured so that the blank correction may be measured once and will remain the same. The blank should, in any case, be checked periodically.

Determination of Cadmium in the Presence of Zinc. Ten milliliters of 6*N* sodium hydroxide, 1.0 ml. of 10% potassium cyanide solution, and 80 ml. of water are added to the titration cell and the blank correction is determined on these reagents as for the calcium in magnesium titrations. The wave length employed in this titration is 236 mμ. After this end point has been passed and recorded, the solution containing the cadmium and zinc is added to the titration cell and the Versenate titration continued as before until the second end point is reached. The amount of cadmium present is equivalent to the difference between these two end points (the blank correction end point and the final cadmium–Versenate end point).

Determination of Zirconium. Ten milliliters of standard Versenate solution and 15 ml. of a sodium acetate solution (0.05 gram of sodium acetate per ml.) are added to the titration cell followed by an aliquot of the zirconium solution. This aliquot should not contain more zirconium than can be chelated with the amount of Versenate added to the solution—i.e., not more than 80 mg. of zirconium per milliequivalent of Versenate added. To the titration cell is then added 1.0 ml. of a 6% salicylic acid solution in acetone, followed by enough water to make the total volume 85 to 90 ml. Then 3*N* ammonium hydroxide is slowly added to this solution with stirring until the pH is adjusted to 4.0. (The amount of 3*N* ammonium hydroxide required for this pH adjustment may be determined on a separate aliquot of the zirconium.) The wave length of the spectrophotometer is set at 520 to 525 mμ and the excess Versenate titrated with standard iron(III) solution using the spectrophotometric end point of the iron(III)–salicylic acid system (*6*). The amount of excess Versenate is obtained from the usual plot of absorbancy *vs.* milliliters of iron(III) added. The zirconium–Versenate complex corresponds to a 1 to 1 ratio of zirconium to Versenate.

DISCUSSION

The results in the standardization of the Versenate solution with standard calcium using a spectrophotometric end point are given in Table I. The average deviation from the mean in both of the standardizations of 0.013 and the 0.0013*M* Versenate is of the order of 0.10%.

The results of the separate determinations of magnesium, cadmium, and zinc in an ammonia–ammonium chloride buffered solution of pH 10 with standard Versenate are given in Table II. The total volume of these metal solutions was between 90 and 100 ml., so that the final solution varied from 0.8 to 100 p.p.m. in the metal ions. The average error for the titration of cadmium, magnesium, and zinc with the 0.013*M* Versenate was about 2 parts per thousand, while for the titrations with 0.0013*M* Versenate the average error was slightly higher (4.5 parts per thousand). The

Table I. Standardization of Versenate Solutions with Standard Calcium Solutions

Calcium		Versenate		Deviation from Mean %
Ml.	Molarity	Ml.	Molarity	
4.987	0.01030	3.840	0.01338	0.03
4.987		3.835	0.01340	0.10
4.987		3.838	0.01338	0.05
10.015		7.728	0.01335	0.25
10.015		7.697	0.01340	0.16
4.987	0.001008	3.808	0.001320	0.05
4.987		3.806	0.001320	0.05
10.015		7.637	0.001321	0.03
10.015		7.628	0.001323	0.17
10.015		7.643	0.001320	0.05
10.015		7.646	0.001320	0.05

precision in these titrations was much better than indicated by the average error figure.

Although a study was not made of the interferences from other cations in the determination of calcium, magnesium, cadmium, and zinc, these interferences could be divided into two classes: those compounds that did not chelate with Versenate but which showed large absorbances at the wave lengths used, and those compounds that do form stable chelates with Versenate. The first type of interference would be evident as soon as the cation solution was added to the titration cell by the inability to obtain a zero absorbancy reading. If only small amounts of these interferences were present, so that the absorbancy reading was not greatly increased, this type of interference would not cause trouble. Many of the transition elements have strong absorbances at these wave lengths and would thus interfere when present in large amounts.

Table II. Determination of Magnesium, Cadmium, and Zinc with Standard Versenate

Cation	Molarity of Versenate	Sample, Mg.		Error, %
		Taken	Found	
Magnesium	0.01338	2.062	2.058	0.11
		2.062	2.057	0.24
		2.062	2.056	0.29
	0.001321	0.2062	0.2061	0.05
		0.2062	0.2069	0.34
		0.2062	0.2074	0.58
		0.0830	0.0837	0.91
Cadmium	0.01338	10.84	10.80	0.34
		10.84	10.87	0.24
		10.84	10.87	0.25
		10.84	10.87	0.25
	0.001321	1.089	1.082	0.64
		1.089	1.084	0.46
Zinc	0.01338	6.210	6.210	0.00
		6.210	6.223	0.21
		6.210	6.219	0.14
		6.210	6.228	0.29
	0.001321	0.6210	0.6224	0.24
		0.6210	0.6232	0.35

Interfering metals of the second class would chelate with the excess Versenate, thus preventing the HY^{---} and Y^{----} Versenate anions from indicating the end point. In many cases, however, these interferences may be avoided by the addition of cyanide or other complexing agents to the titration cell.

In strongly alkaline solutions, calcium may be titrated with Versenate without interferences from magnesium. Cheng *et al.* (*1*) have made use of this in the determination of calcium in limestone using murexide as indicator. The murexide end point in strongly alkaline solutions is, however, not as distinct as the Eriochrome Black T end point in ammonia solutions. The spectrophotometric procedure, on the other hand, not only gives a very sharp end point for the titration of calcium in the presence of magnesium but may also be used for the determination of cadmium in the presence of zinc when similar alkaline solutions are employed.

In the determination of calcium in the presence of magnesium, the final solution should be approximately 0.6*N* in sodium hydroxide. Sodium hydroxide was found to be much superior to potassium hydroxide. When larger amounts of magnesium are present, the results of the calcium titrations are always low. This error is undoubtedly due to the coprecipitation or adsorption of the calcium on the precipitated magnesium hydroxide. The addition of citric acid to the calcium-magnesium solution decreases this error considerably, although even with citrate present the titration of 2 mg. of calcium in the presence of 2 mg. of magnesium was 1.3% low. This error is, however, relatively constant for given amounts of calcium and magnesium, so that a correction could be made for this error. Because of the amounts of sodium hydroxide and citric acid present, a considerable blank is caused by the impurities even when reagent grade chemicals are used. It is therefore important to run a blank on the reagents. The results of the titrations of calcium in the presence of magnesium are given in Table III.

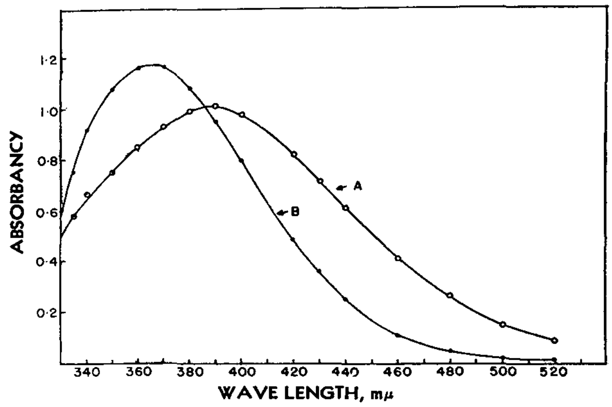

Figure 3. Spectra of Titanium-Peroxide-Versenate Systems

A. **1.01 × 10^{-3} *M* titanium, 0.3% hydrogen peroxide, and pH 1.7**
B. **1.01 × 10^{-3} *M* titanium, 0.3% hydrogen peroxide, 1.33 × 10^{-3} *M* Versenate, and pH 1.7**

In strongly alkaline solutions (0.6*N* sodium hydroxide) zinc will form the zincate ion which is not chelated with Versenate. Cadmium precipitates in alkaline solutions as the hydroxide which shows no amphoteric properties. If this hydroxide precipitate is prevented by the addition of a small amount of cyanide, it is then possible to titrate alkaline cadmium solutions with Versenate without interference from considerable amounts of zinc. The results of the determination of cadmium in the presence of zinc are given in Table IV.

Although the determination of zirconium with Versenate involves a back-titration of the excess Versenate with iron(III) solution, it is as fast as a direct titration and is one of the few volumetric methods for zirconium. The iron–salicylic acid end point at a wave length of 520 to 525 mμ gives a very sharp titration curve that requires very few absorbancy readings in order to extrapolate back to the exact end point. The optimum pH for the titrations is 4.0. In the titrations of zirconium that were carried out at pH levels between 1.0 and 2.0 the results were consistently low, although there seems to be little tendency for the iron(III) to displace Versenate from the zirconium-Versenate chelate. The results of the zirconium titrations are given in Table V.

Titrations similar to the back-titrations of zirconium were tried on titanium(IV) solutions. However, in the back-titration of the excess Versenate with iron(III) solution, the iron(III) not only chelated with the excess Versenate, but also displaced the Versenate from the titanium-Versenate chelate. This displacement was rather slow, requiring 10 to 20 minutes for equilibrium to be reached when the solution had a pH of 2, and even longer periods

Table III. Determination of Calcium in Presence of Magnesium

Calcium, Mg.		Magnesium Added, Mg.	Error %
Taken	Found		
2.014	2.013	0.00	0.05
2.014	2.016	0.41	0.10
2.014	2.017	0.83	0.15
2.014	1.984	2.07	1.49
2.014	1.990	2.07	1.19
2.014	1.986	2.07	1.39
2.014	1.979	4.14	1.73
4.044	4.052	0.41	0.21
4.044	4.011	2.07	0.82
4.044	3.991	4.14	1.31
4.044	4.035	0.00[a]	0.22

[a] 3.10 mg. of zinc added.

of time at a pH of 4. At least 99% of the Versenate was displaced from the titanium-Versenate chelate at a pH of 2.

It was possible to titrate zirconium in the presence of smaller amounts of titanium with a fair degree of accuracy if equilibrium was reached in the back-titration with iron(III) before recording the absorbancy readings. However, the time required for such a titration was over 30 minutes, and the results indicated the necessity of a carefully standardized procedure for satisfactory results. For example, after excess Versenate was added to a solution containing 1.94 mg. of titanium(IV) and 5.164 mg. of zirconium, the pH was adjusted to 4.0 and the excess Versenate was back-titrated with standard iron(III) solution. The amount of zirconium found was 5.197 mg., or an error of 0.64%.

On the other hand, if, during the back-titration of the excess Versenate in a similar solution of titanium and zirconium, 1 ml. of excess iron(III) was added and this solution was allowed to stand 30 minutes before titrating the excess iron, the zirconium found was 6.3% low. There is also a tendency for the titanium to precipitate from solution after the iron has displaced the Versenate from the titanium-Versenate chelate, so that the absorbancy readings are not too stable.

Table IV. Determination of Cadmium in Presence of Zinc

Cadmium, Mg.		Zinc Added, Mg.	Error, %
Taken	Found		
11.06	11.05	0.00	0.09
11.06	11.03	0.00	0.27
11.06	11.02	0.00	0.36
5.508	5.483	0.00	0.45
11.06	11.05	3.10	0.09
11.06	11.07	3.10	0.09
11.06	11.05	6.20	0.09
11.06	11.02	50.0	0.36
11.06	11.03	50.0	0.27

In an effort to reduce the stability of the titanium-Versenate chelate further, hydrogen peroxide was added to the titanium solution. It was hoped that by forming the titanium peroxide complex the titanium-Versenate chelate would not form and no new chelate containing Versenate would be produced. However, when an excess of Versenate was added to an acid titanium solution containing 0.3% hydrogen peroxide and the pH of this solution was adjusted to 2 to 4, iron(III) was able to react only with the excess Versenate. The titanium-Versenate chelate in the presence of hydrogen peroxide was now stable enough to prevent the iron(III) from displacing the Versenate from this complex. The amount of titanium found by this method, however, was slightly low (0.7 to 1.5%), indicating that perhaps a small amount of the Versenate was still displaced by the iron(III).

The spectra of the titanium-peroxide system and the titanium-hydrogen peroxide–Versenate system (Figure 3) showed that the normal titanium–hydrogen peroxide maximum of 390 mμ (pH 1.7) was shifted to a wave length of 365 mμ but the shape of the curve remained the same. This would indicate that the titanium-peroxide complex was capable of reacting with Versenate to form another complex ion that contained titanium, peroxide, and Versenate. Furthermore, from the titrations it was apparent that the titanium–hydrogen peroxide–Versenate complex or chelate was more stable than the original titanium-Versenate chelate.

It was possible to follow the course of the formation of the titanium–hydrogen peroxide–Versenate complex by a spectrophotometric titration of a titanium–hydrogen peroxide solution with Versenate at a wave length of 450 mμ and at a pH of 1.9 (hydrogen peroxide concentration was 0.3%). This titration gave a good titration plot and an end point that corresponded to a complex having a one to one titanium to Versenate ratio.

Table V. Titration of Zirconium with Standard Versenate

Zirconium, Mg.		Error, %
Taken	Found	
5.164	5.163	0.02
5.164	5.144	0.39
5.164	5.129	0.67
5.164	5.147	0.33
5.164[a]	5.010[a]	3.0
5.164[a]	5.037[a]	2.5

[a] pH of final solution was 1.2.

Although titanium can be determined when hydrogen peroxide is present by either a direct titration with Versenate using a wave length of 450 mμ or by a back-titration of excess Versenate with iron(III), there seem to be few advantages of these methods over other existing volumetric and photometric procedures for titanium.

ACKNOWLEDGMENT

The financial aid of a predoctoral fellowship to the first author from the Eastman Kodak Co. is gratefully acknowledged.

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Picrates of Alkylpyridines—Correction

Work subsequent to the publication of "Picrates of Alkylpyridines. Identification by X-Ray Diffraction Powder Patterns" [Janz, G. J., and Solomon, Raymond, ANAL. CHEM., **25**, 454, 1775 (1953)] has shown that the data cannot be used as standards of reference. The target of the chromium tube suffered contamination with tungsten and iron. Thus, rather than monochromatic Cr-K$_{\alpha}$ radiation, the spectrum contained, in addition, the Cr-K$_{\beta 1}$, Fe-K$_{\alpha}$, Fe-K$_{\beta 1}$, and W-L$_{\alpha}$, W-L$_{\beta 1}$, W-L$_{\beta 2}$ lines. The powder patterns contained many extraneous lines leading to erroneous values for the interplanar spacings, and relative intensities. While these data can readily be corrected for the erroneous *d* spacings, it is not possible to correct the relative intensities of the lines. Further work, using pure Cr-K$_{\alpha}$, or Cu-K$_{\alpha}$ radiation is necessary if data for use as absolute reference standards for the alkylpyridine picrates are desired.

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Spectrophotometric Determination of Iron in Vanadium, Chromium, Manganese, Nickel, and Zinc

1,10-Phenanthroline Rate Phenomena

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The wide extent of iron impurities in metals and their salts frequently necessitates determining trace quantities of iron. As spectrographic methods are often inconvenient, requiring time-consuming preparations of new procedures and working curves, the spectrophotometric ferroin procedure is often favored. In this work the ferroin method is applied to new systems by utilization of differing kinetic rates and extraction techniques. The slow rate of reaction of vanadium, chromium, and nickel with 1,10-phenanthroline permits quantitative formation of the tris(1,10-phenanthroline)iron(II) ion, which is then extracted as the perchlorate salt into a nitrobenzene phase, in which its absorbance is determined. Reaction rates of the first transition series metal ions with 1,10-phenanthroline are classified and deviations from recent theoretical approaches discussed. Rapid, sensitive, and accurate procedures are given for determination of γ to 200 γ of iron in vanadium, chromium, manganese, nickel, and zinc. The ferroin perchlorate extraction technique should be applicable to other systems as well as those considered here.

THE spectrophotometric determination of iron as the tris-(1,10-phenanthroline)iron(II) ion (ferroin) has had limitations because of the interference of highly colored solutions as well as the reaction of cations other than iron with 1,10-phenanthroline (*15*). Elements of the first transition series especially have presented difficulties in iron analysis. There is a need for a rapid and accurate method of determining traces of iron in these metals and their salts.

In the present work extraction techniques, differing kinetic rates, and competitive complexing are used to extend the spectrophotometric ferroin analysis to the elements of the first transition series with the exception of copper and cobalt. In determining trace amounts of iron in vanadium, chromium, and nickel, the usual interferences are circumvented by the extraction of ferroin as the perchlorate salt into a nitrobenzene phase. The ferroin absorbance is measured in the nitrobenzene. With vanadium, chromium, and nickel solutions, extraction makes it possible to utilize the faster rate of formation of ferroin as compared to vanadium–, chromium–, and nickel–1,10-phenanthroline complexes to separate and determine iron.

The determination of iron in manganese is possible owing to the greater stability of ferroin compared to that of the manganese–1,10-phenanthroline complex. The zinc ammine complex is utilized to allow formation of ferroin in the presence of large quantities of zinc. Extraction is unnecessary with manganese and zinc.

Ferroin forms a water-insoluble perchlorate salt (*15*) which is extractable into organic solvents of high dielectric constant. Chloroform will quantitatively remove ferroin perchlorate from the aqueous phase, but it requires several extractions and on standing the ferroin perchlorate slowly precipitates from the chloroform solution. Nitrobenzene is far more satisfactory than other extractants. Its high distribution coefficient permits quantitative removal of ferroin perchlorate from the aqueous phase in one extraction. It equilibrates with extreme rapidity, requiring only a few seconds shaking. The spectrum of ferroin perchlorate is altered in nitrobenzene from its spectrum in water or chloroform. There is a 5-mμ shift of the absorbance maximum to longer wave length and a 13.5% increase in the molar absorptivity.

Table I summarizes the initial interferences of the elements in applying the spectrophotometric ferroin method and how these interferences are overcome. However, iron still cannot be determined in the presence of large amounts of cobalt or copper. Milligram quantities of copper could be removed by extraction with 2,9-dimethyl-1,10-phenanthroline (*14*). If greater sensitivity for iron is desired 4,7-diphenyl-1,10-phenanthroline might be used.

APPARATUS

Absorbance measurements were made with a Beckman Model DU quartz spectrophotometer and a Cary Model 12 recording spectrophotometer. A Beckman Model G pH meter was used for pH measurements. Squibb-type separatory funnels, 250-ml. capacity, equipped with Teflon stopcock stoppers and 25-ml. glass-stoppered Erlenmeyer flasks were used for all extractions. The Teflon stoppers were obtained from Kontes Glass Co., Vineland, N. J.

Table I. Spectrometric Determination of Trace Amounts of Iron in Vanadium, Chromium, Manganese, Nickel, and Zinc

Ion	Classification of Observed Rate with Ph[a]	Nature of Interference with Ferroin Method	Factors to Overcome Interferences	Medium of Absorbance Measurement
V(IV)	Inert (mono)[b]	Color, Ph reaction	Kinetic, extraction	Nitrobenzene
Cr(III)	Inert	Color	Extraction	Nitrobenzene
Mn(II)	Labile	Ph reaction	Excess Ph	Water
Fe(II)	Inert (tris)[b]	......	....	....
Fe(III)	Labile	......	....	....
Co(II)	Labile	Color, Ph reaction	None	....
Ni(II)	Inert (mono, bis, tris)[b]	Color, Ph reaction	Kinetic, extraction	Nitrobenzene
Cu(I)	Labile	Color, Ph reaction	None	....
Cu(II)	Labile	Color, Ph reaction	Neo-cuproine	Nitrobenzene
Zn(II)	Labile	Ph reaction	NH_3 complex	Water

[a] 1,10-Phenanthroline.

[b] Parentheses indicate slow-forming complexes.

REAGENTS

All chemicals used were reagent-grade quality.

1,10-Phenanthroline solution, 0.1%.

Hydroxylammonium chloride solution, 10%.

Sodium perchlorate solution, 1*M*.

DISCUSSION

Ferroin is classified according to Taube's system (*16*) as an inert inner orbital complex, meaning that it uses the 3*d* orbitals for octahedral bonding and has a measurable rate of formation and dissociation. It has a half life of 2.5 hours when placed in an environment favoring its dissociation. Its rate of formation is extremely rapid, as it has a formation constant equal to 10^{19} min.$^{-1}$ (*11*). It is a very stable complex whose pK equals 21.3 (*10*).

In the transition series elements, zinc(II), copper(I), and copper(II) would be expected to form labile outer orbital complexes with 1,10-phenanthroline since all their 3*d* orbitals are already occupied. Qualitative observations confirm that their rates of reaction with 1,10-phenanthroline are faster than iron(II). Nickel(II), however, despite the presence of eight electrons in the 3*d* orbitals, reacts slowly with 1,10-phenanthroline. Even the formation of the mono(1,10-phenanthroline)nickel(II) ion is significantly slower than ferroin formation. Indeed it is sufficiently slow to allow quantitative separation of traces of iron from nickel.

These observed inert nickel complexes have been confirmed by the thorough study in this field by Basolo, Hayes, and Neumann (*1*). They report stable mono-, bis-, and tris-1,10-phenanthroline complexes with nickel—all inert complexes. According to Taube (*16*), nickel ion very likely promotes two of its 3*d* electrons to the 4*d* level in order to form an inner orbital complex. Burstall and Nyholm (*3*), in studying the very similar dipyridyl complexes of nickel, reach the conclusion that the 3*d* electrons are not promoted since the promoted electrons would be found paired in the 5*s* orbital yielding a diamagnetic susceptibility. Magnetic susceptibility studies of the nickel 1,10-phenanthrolines being conducted in this laboratory indicate two unpaired electrons for all three nickel complexes. Martell and Calvin (*12*) incorrectly report a diamagnetic bis(1,10-phenanthroline)nickel(II) complex apparently from a mistranslation of the work of Cambi (*4*).

Iron(III) and manganese(II), with the stable electronic configuration of a half-filled 3*d* level, apparently form labile outer orbital complexes with 1,10-phenanthroline. The reaction rates of iron(III) and manganese(II) are faster than iron(II) and their complexes are much weaker (*7, 8*). Magnetic data also indicate outer orbital complexing (*4*). Chromium(III) forms an inert inner orbital complex with 1,10-phenanthroline. However, the chromium(III) complex has a very slow rate of formation so that it offers no appreciable competition to iron(II).

According to Taube's generalization (*16*), vanadium(IV) would not be expected to form an inert inner orbital complex, as it has less than three electrons in the 3*d* orbitals. Yet the 1,10-phenanthroline complex of vanadium(IV) is slow to form and to dissociate. No previous report has been made of vanadium(IV) complex ions inert to substitution. Vanadium chemistry is complicated by its oxygen, hydroxyl, and polymerized species. Nevertheless the slow substitution reactions of the mono(1,10-phenanthroline)vanadium(IV) ion suggest an inert complex.

This apparent contradiction to Taube's postulate, using electronic configuration to explain the inert and labile complexes, might be explained in other ways. First, the double bond character of the vanadium-oxygen bond in the VO^{++} ion as distinguished from $V(OH)_2{}^{++}$ (*6*) could cause three of the 3*d* orbitals to be occupied. This would mean stability of the VO^{++} ion in a manner similar to $UO_2{}^{++}$ (*5*). Second, the use of orbitals such as $3d^44s4p$ for bond formation could give a trigonal prism rather than octahedral arrangement to account for an inert complex. Third, polymerization of the vanadium(IV) species in aqueous solution could account for slow reactions. Further investigation of this problem is being conducted.

The observed classification of the 1,10-phenanthroline complexes is summarized in Table I. This information has been utilized in developing analytical procedures for the determination of iron.

EXPERIMENTAL

Vanadium. Since vanadium in the penta- and trivalent states forms precipitates with 1,10-phenanthroline, the vanadium for analysis is oxidized or reduced to the quadrivalent state by the addition of hydroxylammonium chloride. Hydroxylamine appears to form a strong complex with vanadium(IV), which at pH 5 gives a completely colorless solution. The color of the vanadium-hydroxylamine system is pH-dependent, changing in sequence from blue to colorless to yellow as the pH is varied from 4 to 7. The blue to colorless change with pH appears to involve no reduction.

A Job's method plot (*17*) of spectrophotometric data, from varying the 1,10-phenanthroline and vanadium concentrations at a constant total molar concentration of 3.55×10^{-4} in the presence of hydroxylamine at pH 4, showed the existence of a 1 to 1 complex which is assumed to be mono(1,10-phenanthroline)-vanadium(IV) ion. No evidence was found for additional 1,10-phenanthroline complexes. The perchlorate salt of this complex does not extract into chloroform or nitrobenzene.

The rate of formation constant of the mono(1,10-phenanthroline)vanadium(IV) ion is on the order of 10^4 *min.*$^{-1}$, assuming a second-order reaction. The value of the dissociation constant as estimated by chloroform extraction of the unreacted 1,10-phenanthroline is less than 10^{-6}. Compared with the rate of formation constant of 1.3×10^{19} min.$^{-1}$ for ferroin (*11*) the vanadium reaction is slow, so that initially all the iron will react with the 1,10-phenanthroline. An extraction of ferroin perchlorate is then performed before the ferroin can dissociate to form mono(1,10-phenanthroline)vanadium(IV) ion.

PROCEDURE. After solution of the vanadium compound containing about 0.25 gram of vanadium (nitric acid may be used for vanadium metal), 20 ml. of the hydroxylammonium chloride solution are added. Five to 10 minutes are allowed for the vanadium to react with the hydroxylamine. Ammonia is added until the solution is colorless (pH 4 to 5), and the solution is transferred to a 250-ml. separatory funnel. One milliliter of the sodium perchlorate solution and 20 ml. of the 1,10-phenanthroline solution are added. Exactly 20 ml. of nitrobenzene are added within 2 minutes of the 1,10-phenanthroline addition. The funnel is shaken vigorously for 30 seconds.

After the phases have separated, 20 ml. of 1,10-phenanthroline solution are added and the extraction is repeated to ensure complete removal of all iron. The lower nitrobenzene layer is drawn off into a 25-ml. glass-stoppered Erlenmeyer flask containing 1 to 2 grams of anhydrous sodium sulfate crystals. The flask is shaken for several minutes to dry the nitrobenzene before reading the absorbance on the spectrophotometer at 515 mμ.

Since water affects the nitrobenzene absorbance and iron impurities in reagents are common, it is always important to run a blank. Nitrobenzene vapors are toxic. The operations with it should be carried out in a hood. A calibration curve should be constructed. One absorbance unit per centimeter = 86.4γ of iron.

Chromium. Chromium reacts to form a number of 1,10-phenanthroline complexes (*13*), but ferroin forms rapidly in the presence of large amounts of chromium(III). The intense absorbance of the chromium ion necessitates extraction of the ferroin for spectrophotometric determination. A pH range of 2 to 3 is recommended for complete ferroin formation. Time of extraction after the 1,10-phenanthroline addition is not critical as the competitive chromium reaction is very slow.

PROCEDURE. After solution of the chromium sample containing about 0.5 gram of chromium, 10 ml. of hydroxylammonium chloride solution, 20 ml. of 1,10-phenanthroline solution, and 1 ml. of sodium perchlorate solution are added and the pH is adjusted to 2 to 3. The solution is extracted with exactly 20 ml. of nitrobenzene, the extract is drawn off and dried, and the absorbance is read at 515 mμ as in the vanadium procedure.

Manganese. Ferroin forms slowly in the presence of excess manganese(II) because of the prior formation of what is thought to be the mono(1,10-phenanthroline)manganese(II) ion. The manganese complex is much weaker than the iron(II) complex. It forms and dissociates rapidly. Ferroin absorbance is measured in the manganese solution at pH 2 to 3. Higher pH causes slow decomposition of the ferroin yielding a green solution.

PROCEDURE. Ten milliliters of hydroxylammonium chloride solution, 1 ml. of sodium perchlorate solution, and 20 ml. of 1,10-

phenanthroline solution are added to the solution of the manganese sample containing about 0.5 gram of manganese. The pH is adjusted to 2 to 3 and the solution diluted to 100 ml. The absorbance is read at 510 mμ.

Nickel. The mono-, bis- and tris-1,10-phenanthroline complexes of nickel have been reported (*1*). All have measurably slow rates of formation. Advantage can be taken of the fact that the rate of formation of mono(1,10-phenanthroline)nickel(II) ion is significantly slower than the rate of formation of ferroin to determine iron in nickel as in vanadium. However, the determination is more difficult, since the rate of formation of nickel is faster than that of vanadium with 1,10-phenanthroline.

As the iron concentration is decreased, a point may be reached, depending on the amount of excess 1,10-phenanthroline added, where the rate of formation of the mono(1,10-phenanthroline)nickel(II) ion, k_{Ni}, exceeds the rate of formation of tris(1,10-phenanthroline)iron(II) ion, k_{Fe}. If these rates are equal:

$$[\mathrm{Fe}^{++}]_{aq} = k_{\mathrm{Ni}}/k_{\mathrm{Fe}} \times [\mathrm{Ni}^{++}]/[\mathrm{Ph}]^2$$

where Ph is the concentration of 1,10-phenanthroline

Thus, the greater the nickel concentration and the higher the acidity (formation of the phenanthrolium ion), the greater the amount of iron left in the aqueous phase and not extracted as ferroin perchlorate.

At higher pH an extractable nickel-nitrobenzene species with an absorption maximum at about 460 mμ distinct from the nickel phenanthroline spectra interferes with the nitrobenzene extraction of ferroin perchlorate; hence pH 3 is recommended. Short extraction periods help to minimize the extent of nickel extraction. The determination of iron in nickel is further complicated by the nickel and nickel-1,10-phenanthroline complexes extracted into the nitrobenzene. The nickel continues to react with 1,10-phenanthroline in the nitrobenzene phase causing dissociation of the extracted ferroin. This dissociation may be prevented by adding an excess of 1,10-phenanthroline crystals to the nitrobenzene extract.

The size of the nickel sample should be kept to a minimum. Using identical quantities of 1,10-phenanthroline, a linear calibration curve may be constructed for varying amounts of iron in a given weight of nickel sample without actually achieving complete iron removal as ferroin. For isolated samples, several additions of a large excess of 1,10-phenanthroline will ensure quantitative formation of ferroin.

PROCEDURE. A 0.1-gram nickel sample is dissolved, 10 ml. hydroxylammonium chloride solution and 1 ml. sodium perchlorate solution are added, and the pH is adjusted to 3. The solution is transferred to the separatory funnel, and 20 ml. of 1,10-phenanthroline solution are added and followed immediately by the addition of 20 ml. of nitrobenzene. After 30 seconds of vigorous shaking, the nitrobenzene layer is drawn off and the procedure repeated with more 1,10-phenanthroline and nitrobenzene. A total of 50 ml. of 1,10-phenanthroline solution is used, and the nitrobenzene extracts are diluted to a 50-ml. volume. A few 1,10-phenanthroline crystals are added to the nitrobenzene extract. Extract is dried and absorbance read at 515 mμ as before. Reproducible results are ensured and calibration curve is constructed.

Zinc. From the reported constants of zinc– and iron–1,10-phenanthroline complexes (*9*) and the zinc ammine complex (*2*), it is possible to estimate the necessary pH and ammonium ion concentration to ensure quantitative formation of ferroin in the presence of large quantities of zinc. 1,10-Phenanthroline and ammonium chloride are added first, and then the pH is adjusted with ammonium hydroxide to pH 9.

The use of the ammine complex of nickel, cobalt, and copper to permit ferroin formation in a manner similar to that for zinc is not possible. Cobalt and copper ammines do not sufficiently prevent the reaction of these ions with 1,10-phenanthroline. The ammoniacal nickel solution causes reaction between nickel and nitrobenzene and hence extraction of interfering species.

PROCEDURE. After solution of the 0.5-gram zinc sample, 10 ml. of hydroxylammonium chloride solution, 30 ml. of 4*M* ammonium chloride solution, and 20 ml. of 1,10-phenanthroline solution are added. The pH is brought to 9 with ammonium hydroxide and the solution diluted to 100-ml. volume. The absorbance is read at 510 mμ.

Table II. Determination of Iron

Element, Gram	Iron, γ Added	Iron, γ Found	Element, Gram	Iron, γ Added	Iron, γ Found
V, 0.25	20.0	20.1	Mn, 0.5 (*Contd.*)	200.6	200.1
	50.0	50.3		401.2	402.4
	70.0	69.8	Ni, 0.1	25.0	24.5
	100.0	97.5		75.0	72.3
Cr, 0.5	80.2	83.5		150.0	148.0
	100.4	100.9	Zn, 0.5	100.2	100.0
	200.2	200.5		300.6	300.4
Mn, 0.5	40.1	40.1		501.0	501.2
	140.4	140.0			

Cobalt and Copper. The rapidity of the reaction rate of these elements with 1,10-phenanthroline and the strength of the complexes formed prevent the direct use of 1,10-phenanthroline for iron determination in their presence. In the above procedures, up to 2 mg. of either element give no interference, provided the pH is low enough (below 5) to prevent hydroxylamine from reducing the copper to the cuprous state. If sufficient 1,10-phenanthroline is added, copper(II) may be extracted simultaneously with ferroin and its absorbance read at 760 mμ, with very little interference at 515 mμ. Neo-cuproine (*11*), 2,9-dimethyl-1,10-phenanthroline, could be used to determine quantitatively and remove small amounts of copper before the addition of 1,10-phenanthroline.

Table II presents iron analyses using the above procedures. A calibration curve was used for nickel. This extraction technique for ferroin perchlorate ought to extend the applicability of the spectrophotometric ferroin method to other systems not considered in the present work. It can well be applied for the determination of iron in any darkly colored solutions in which ferroin forms and in the presence of any other metal ions which react slowly with 1,10-phenanthroline.

The exceptions found in the cases of vanadium and nickel to Taube's otherwise widely applicable classification of reaction rates are under further investigation.

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Spectrographic Analysis of Minor Elements Extracted from Plants and Soils as Dithizonates

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The spectrograph makes possible determination of several elements in a single exposure. When spectrographic technique is applied to the determination of minor elements in plants and soils, the variability of the base material hampers quantitative work. Chemical separation of the minor elements is required previous to spectrographic determination. In the method described cobalt, zinc, and copper are separated from soils or plant ash in the form of dithizonates. Spectrographic determination of the dithizonates is made in the ranges 0.1 to 100γ for cobalt, 0.3 to 100γ for copper, and 10 to 100γ for zinc. The reproducibility of the determinations gave a standard deviation of ±5% for cobalt, ±9.2% for zinc, and ±15% for copper. The sensitivity and accuracy of the method are at an adequate level for any practical quantitative problem involving these trace elements in agriculture.

THE physiological role of the micronutrient elements cobalt, copper, zinc, molybdenum, boron, iron, and manganese in plants and animals has aroused great interest in recent years. Coincident with this interest, a demand for sensitive, accurate, and flexible methods of quantitative analysis for these elements in widely variable and complex materials has arisen. The adaptation of spectrochemical methods to the determination of these agriculturally important trace elements is strongly indicated when it is realized that every one of these elements can be determined with accuracy and sensitivity in a single exposure using modern spectrographic equipment.

Ordinarily, analytical techniques involving spectrochemical analysis are regarded as more or less self-sufficient, with the spectrograph carrying the major burden of the entire procedure. This is an ideal situation which can only be obtained when the sample frequency is high and variables other than the concentrations under consideration are under reasonable control. Obviously, it is impossible to develop suitable standards to cover all types of soil, soil extracts, fertilizers, and plant tissues without extensive chemical treatment prior to spectrographic analysis. During this development it is inevitable that the spectrograph will slip from its dominant role to a minor role as a final instrument of determination in a chain of chemical manipulations.

However, the combination of prechemical treatment and spectrographic analysis is a powerful one and is capable of contributing to the solution of quantitative problems associated with trace element nutrition. The average effective concentration of these elements is so low that their combined effect on a spectrochemical procedure can be reduced to insignificance by chemical isolation and concentration followed by recombination in a standard matrix. A similar approach to the problem of the effective use of the spectrograph in determining minor elements in plants and soils is used in the work of Carrigan and Erwin (*1*) and Mitchell and his associates (*2*). In this investigation, the quantitative spectrochemical examination of zinc, cobalt, and copper as dithizonates was devised as the first step in such a procedure.

CHEMICAL PROCEDURE

Representative soil and plant ash samples are dissolved by fusion with anhydrous sodium carbonate, after the method of Mitchell and associates (*2*), using 1-gram samples of soil and the ash from 10 grams of oven-dry tissue for plant samples. An attempt to employ the method of isolation and concentration described by these workers was abandoned in favor of more specific methods.

Spectrographic examination of the dithizonates obtained from a wide variety of soils and plants at the established pH level of 8.3 shows that these consist of copper, cobalt, zinc, lead, silver, tin(II), iron(II), and manganese. As manganese is an element of agricultural importance, an attempt was made to include it in the analytical system. This attempt was a failure because the extractability of manganese appears to be controlled by the excess of citrate added to the sample. If just sufficient citrate is added to prevent the precipitation of the insoluble salts formed at a pH of 8.3, manganese can be extracted. However, if an excess beyond this level is present the extraction of manganese cannot be accomplished. Since the determination of cobalt is required, a definite excess of citrate is recommended because it was experimentally demonstrated that a perceptible turbidity in the solution at a pH of 8.3 was sufficient to cause the complete loss of small amounts of cobalt by coprecipitation. Apart from the minor difficulty of ensuring an excess of citrate in all samples, the chemical procedure is straightforward.

Isolation and Concentration of Copper, Cobalt, and Zinc. Evaporate the solution containing the trace elements to approximately 150 ml., add 20 ml. of 40% ammonium citrate, and adjust the pH to 8.3 with ammonium hydroxide. Transfer the solution to a 250-ml. separatory funnel and extract with 10-ml. portions of 0.10% dithizone in chloroform until all the complex-forming metals have been separated, collecting the extracts in a 50-ml. beaker.

The end point can be determined by obtaining a partition between the excess dithizone dissolved in the alkaline aqueous phase and a wash solution of chloroform which will be colored green when the process is complete. This criterion is employed because of the dark color of a 0.10% solution of dithizone which makes it difficult to recognize the end point colorimetrically.

Reagents. All reagents involved in the procedure were used in the highest possible state of purity. Graphite powder, grade SP-2, and spectrochemically pure lithium carbonate were obtained commercially. Distilled water, hydrochloric acid, ammonium hydroxide, and chloroform were redistilled in borosilicate glass circuits. The sodium carbonate and ammonium citrate were purified by preliminary dithizone extractions. Reagent grade dithizone was purified in the manner described by Welcher (*3*).

Despite all these precautions a blank correction for copper of 0.15γ was found necessary in plotting the working curves. No spectrographically detectable disturbance caused by either cobalt or zinc contamination was observed in full blank runs on all reagents combined.

Sample Mounting. Evaporate the chloroform solution of metal dithizonates (in the 50-ml. beaker) to dryness on a steam bath. Dissolve the dry residue in 2-ml. portions of pure chloroform and transfer with chloroform washing to a 10-ml. borosilicate glass beaker containing 100 mg. of high purity, fine-grained graphite. The chloroform wets the graphite and a uniform collector layer forms on the bottom of the beaker.

Evaporate the solution again to dryness with one modification: Direct a jet of air at room temperature onto the outside of the beaker at the boundary line of the collector layer of graphite as the covered beaker is slowly turned at the final stage of evaporation. This prevents the solvent from creeping and ensures complete crystallization on the graphite collector. Place the uncovered beaker in a muffle furnace for 15 minutes at 450° C. This partial ignition is necessary to ensure both reproducibility and agreement with synthetic standards in the subsequent spectrographic analysis.

After ignition, brush the sample out of the beaker and mix with

10 mg. of lithium carbonate. Transfer 50-mg. aliquots of this mixture to a crater bored in a high purity graphite electrode for the final spectrographic examination.

SPECTROGRAPHIC PROCEDURE

Standards. Prepare suitable spectrographic standards by mixing pure oxides in a graphite base in the following manner:

Oxide	Weight Equivalent to 100 Mg. of Metal, Mg.
CuO	125.2
Co_3O_4	136.2
ZnO	124.5
Total	385.9

If the determination of other metals present as dithizonates is required, the appropriate oxides can be combined at this point. Combine these oxides with 1000 mg. of fine-grained, high purity graphite yielding a base standard each 13.859 mg. of which contains 1.0 mg. each of copper, cobalt, and zinc.

Dilute this base standard by adding 900 mg. of graphite to 138.6 mg. of the standard to obtain diluted standard 1 which contains 1.0 mg. each of copper, cobalt, and zinc. This standard is progressively diluted by adding 684-mg. portions of graphite seven times as shown below.

Diluted Standard	Weight of Previously Diluted Standard, Mg.	Amount of Cu, Co, and Zn Resulting from Dilution, Mg.
2	328.2	0.316
3	319.9	0.100
4	317.2	0.0316
5	316.4	0.010
6	316.1	0.00316
7	316.0	0.0010
8	316.0	0.000316

(In this way, each standard is a further dilution of the previously diluted standard. To obtain standard 2, for example, 684 mg. of graphite are added to 328.2 mg. of standard 1. Standard 2 contains 0.316 mg. each of copper, cobalt, and zinc. Standard 2 is then diluted to obtain standard 3 which contains 0.100 mg. each of the elements.)

Finally, add 68.4 mg. of lithium carbonate to each sample with the exception of standard 8 containing 0.000316 mg.; to the latter add 100 mg. and mix thoroughly. Plot the concentrations on the working curves as absolute values with respect to the mixture of graphite and lithium carbonate.

Internal Standard. The agriculturally important trace elements are widely variable in their physical and chemical properties. This consideration made the selection of a suitable internal standard difficult. Selection on an individual basis would complicate the procedure, as each element might require a separate internal standard control for maximum accuracy. After considerable experimental work lithium was selected as the most satisfactory element to give adequate control over the three elements—zinc, cobalt, and copper.

The selection of lithium as the internal standard was indicated by considerations other than internal standardization. The presence of an alkali in the analytical system effectively reduced the carbon background and stabilized the arc. The reproducibility of the system has effectively confirmed the usefulness of lithium in the role of internal standard.

Apparatus. The spectrographic equipment used in the development of this procedure was all commercially available equipment. The spectrograph was a 1.5-meter concave grating instrument recording photographically on 35-mm. film with a dispersion of approximately 6.9 A. per mm. in the first order. The source unit featured a spark-ignited direct current arc source combined with a high voltage spark section. The densitometer was a nonrecording projection comparator type. Established methods of photographic plate calibration, processing, and photometry were employed throughout the procedure. The spectrographic constants used in the system are described herewith.

Spectrographic Constants. SAMPLE FORM, 100 mg. of spectrochemically pure buffer graphite *plus* 10 mg. of spectrochemically pure lithium carbonate plus *x* mg. of partially ignited *zinc, copper*, and cobalt dithizonates thoroughly dried and mixed.

SAMPLE WEIGHT, 50 mg. of mixture per exposure.

UPPER ELECTRODE, a hemispherical tip Grade I graphite electrode, 0.242 inch in diameter.

LOWER ELECTRODE, a Grade I graphite electrode, 0.242 inch in diameter, bored to a depth of $^3/_{16}$ inch, and mounted as the anode containing the sample.

GAP SPACING, 4 mm.

EXPOSURE CONTROL, rotating sector operated by a synchronous motor to reduce the total transmittance to 20%.

FILTERS, one metallized 0.5-inch quartz filter with a 10% transmittance value placed in the optical circuit to reduce the intensity of the copper lines: copper 3247, copper 3273.

EXPOSURE, 1 minute.

SLIT, 40 microns.

GRATING DOORS, adjusted to yield 40% transmittance.

DISCHARGE, a spark ignited, 9.6-ampere direct current arc at 220 volts.

FILM TYPE, SA No. 1.

DEVELOPING TIME, 3 minutes in D-19.

EMULSION CALIBRATION, two-step filtered iron spectrum, one curve covering the range 2400 to 3500 A.

Working Curves. The analytical lines for copper, cobalt, and zinc are all referred to lithium 2562 for internal standard control. The concentration range covered is broad, but it is necessary to cope with the widely variable samples submitted for analysis. Some control over this factor can be exercised in the size of the samples selected for chemical concentration of the trace elements, but it is a definite advantage to have working curves covering as wide a range as possible. Each experimental point upon which the curves are based represent the average of fivefold replication.

The graphical representation of the developed working curves is shown in Figure 1. The minimum sensitivity for each element under the established conditions is approximately 0.10γ for cobalt, 0.30γ for copper, and 10γ for zinc as concentrates. All intensity ratios are calculated without background corrections. The sensitivity of the zinc determination could be increased if necessary by using special conditions and recording the line zinc 2138.5. The spectrograms obtained are not complex, since only the partial spectra of carbon and lithium plus the sensitive lines of the extracted trace elements are recorded.

REPRODUCIBILITY

The method developed for the spectrochemical analysis of copper, cobalt, and zinc dithizonates requires extensive chemical treatment prior to spectrographic analysis; therefore, it was decided to test the reproducibility over the full procedure with

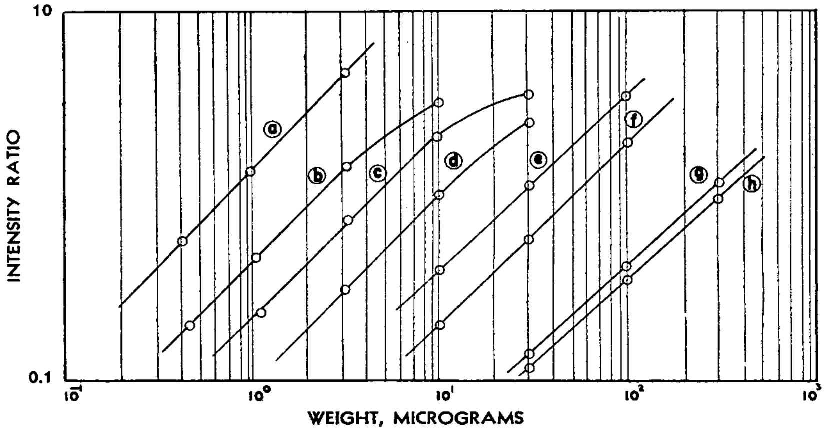

Figure 1. Analytical Curves for Spectrographic Determination of Copper, Cobalt, and Zinc

a. Cobalt 3453
b. Copper 3247
c. Copper 3373
d. Cobalt 3044
e. Cobalt 3388
f. Zinc 3345
g. Zinc 3282
h. Copper 2961

Table I. Reproducibility of Cobalt Determinations in Ashed Alsike

Lab. No.	Transmittance, % Li 2562	Transmittance, % Co 3453	Intensity Ratio	Av.	P.P.M.	Dev., P.P.M.
1	22.3	5.3	2.37	2.34	0.170	0.008
	19.3	4.8	2.31			
2	18.5	4.5	2.30	2.23	0.162	0.000
	17.7	4.8	2.15			
3	17.0	5.2	2.00	2.06	0.150	0.012
	19.5	5.5	2.12			
4	17.0	4.5	2.18	2.22	0.161	0.001
	15.6	3.9	2.25			
5	20.4	5.0	2.31	2.26	0.164	0.002
	20.4	5.4	2.21			
6	15.0	4.4	2.05	2.08	0.151	0.011
	19.0	5.4	2.11			
7	16.7	4.4	2.19	2.21	0.160	0.002
	17.1	4.4	2.22			
8	17.0	4.4	2.20	2.34	0.170	0.008
	19.6	4.2	2.49			
9	20.5	5.3	2.24	2.13	0.154	0.008
	18.7	5.7	2.02			
10	14.0	3.2	2.37	2.39	0.174	0.012
	14.0	3.1	2.41			
				Av.	0.162	

Sample weight = 1.0844 grams

Standard deviation = $\pm\sqrt{\frac{6.10 \times 10^{-4}}{9}} = \pm 0.0082$ p.p.m.

Standard deviation, % = ±5

Table II. Cobalt, Copper, and Zinc in Forage, Oven-Dry Basis

Type	Sample Wt., Grams	Found, P.P.M. Cobalt	Found, P.P.M. Copper	Found, P.P.M. Zinc
Birdsfoot trefoil	10.0	0.11	11.5	27.5
Reed canary grass	10.0	0.07	6.8	19.0
Meadow fescue	10.0	0.20	14.2	23.5
Brome grass	10.0	0.07	15.2	24.0
Brome grass	10.0	0.20	23.0	29.0
Orchard grass	10.0	0.13	30.5	24.5

Table III. Recovery Tests of Cobalt, Copper, and Zinc

(Based on duplicate spectrographic values)

Cobalt, γ Added	Cobalt, γ Recovered	Copper, γ Added	Copper, γ Recovered	Zinc, γ Added	Zinc, γ Recovered
100.0	103.0	100.0	100.0	100.0	100.0
	96.0		100.0		115.0
	103.0		103.0		105.0
	95.0		103.0		105.0
	100.0		107.0		103.0
	96.0		107.0		101.0
30.0	27.0	30.0	33.0	30.0	25.0
	31.0		33.0		30.0
	31.0		33.0		29.0
	32.0		33.0		32.0
	26.0		31.0		27.0
	29.0		31.0		30.0
10.0	10.0	10.5	10.0	10.0	12.0
	11.0		10.0		13.0
	10.0		9.5		13.0
	10.0		10.5		10.0
	10.0		9.5		11.0
3.00	3.00	3.54	3.80		
	2.90		3.90		
	2.80		3.70		
	2.90		3.70		
	3.10		4.10		
	3.00		4.10		
1.00	0.95	1.54	1.70		
	0.96		1.57		
	1.00		1.62		
	0.97		1.65		
	1.07		1.87		
	1.05		1.70		
0.30	0.33	0.84	0.80		
	0.33		0.80		
	0.38		0.90		
	0.38		0.86		
	0.36		0.88		
	0.37		0.84		

the exception of primary sampling. In order to achieve this, the following method was adopted:

A random 100-gram sample of finely ground oven-dry alsike was ashed at 450° C. for 6 hours. The ash obtained was mixed, weighed, and divided into 10 equal portions. These portions were then independently fused, dissolved, extracted, and prepared for spectrographic analysis in the manner outlined.

The details obtained in the analysis for cobalt are contained in Table I. The standard deviations obtained for zinc and copper in the same test were ±9.2 and ±15%, respectively.

ACCURACY

In order to obtain a measure of the accuracy with which the outlined method can be employed the following procedure was used. The results of this analysis are shown in Tables II and III.

Six 10-gram samples of different forage types were analyzed for cobalt, copper, and zinc by the method described. When the dithizonates had been completely removed from solutions of the above samples, volumetric additions of copper, cobalt, and zinc solutions in known concentrations were made to the solutions obtained from each forage type. These additions were made over a wide concentration range, then were independently extracted and spectrographically analyzed.

The relatively high recovery values obtained for cobalt at a concentration of 0.30γ indicates that a correction of approximately 0.05γ might be valid. However, as no evidence for this correction from blanks on the reagents or graphite could be obtained, the results were accepted as indicated.

DISCUSSION

The complications introduced by coextractions using dithizone as an analytical reagent are circumvented by spectrographic examination of the dithizonates. Interference problems are eliminated by line selection on appropriate spectrograms. The sensitivity, reproducibility, and accuracy of the method are at an acceptable level for investigations on the concentration range of the agriculturally important trace elements, copper, cobalt, and zinc, in plants, soils, and soil extracts. The method can be readily extended to include all elements extracted in traces by dithizone under the analytical conditions described.

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Extraction and Recovery of Thiols from Petroleum Distillates

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The study of sulfur compounds in crude oils requires methods for separating the various types of sulfur compounds quantitatively from petroleum distillates. This report describes the qualitative testing and quantitative application of a method for thiols (mercaptan) using sodium aminoethoxide in ethylenediamine solution. This method has been successfully used in the separation of thiols from a distillate boiling between 111° and 150° C.

THE research program of American Petroleum Institute Research Project 48A being conducted at the Petroleum Experiment Station of the Bureau of Mines is concerned in part with the separation and identification of the sulfur compounds in petroleum. A general procedure for separations has been devised which includes isolation of the sulfur compounds from a petroleum distillate by adsorption, fractional distillation in a semimicro column, and identification of the components by infrared absorption spectra and through chemical derivatives. This scheme is satisfactory for a distillate boiling below 100° C., but above this temperature the number of compounds present becomes so large that it is necessary to devise methods of further separating the mixture into types, each of which may then be distilled and studied separately. Such a method for separating and recovering thiols has been developed.

Several methods are described in the literature for the chemical separation of thiols (*1*, *2*), but because of solubility limitations, or possible decomposition or rearrangements, they did not meet the requirements of this project. Thus, aqueous sodium and potassium hydroxides are effective only on the lowest boiling members of the series and on aromatic thiols having the thiol group attached to the ring or in an alpha position with respect to the ring. Heavy metal mercaptides have been used as a means of isolation, but these are gelatinous and difficult to handle and purify, as they adsorb large amounts of other substances. Some metal mercaptides, particularly those of silver, are sensitive to light.

EXPERIMENTAL

The thiol-containing distillate, preferably concentrated by adsorption, is diluted with isopentane (2-methylbutane) and brought in contact with sodium aminoethoxide ($H_2NC_2H_4ONa$) dissolved in anhydrous ethylenediamine ($H_2NC_2H_4NH_2$). From this treatment an extract of sodium mercaptides dissolved in the ethylenediamine is obtained. The thiols are regenerated from this solution by acid hydrolysis and recovered by steam distillation.

The method of Moss, Elliott, and Hall (*3*) for titration of phenols and other weak acids in ethylenediamine suggested the use of this reagent for extraction of thiols. Solutions of sodium hydroxide (up to 50% aqueous) in ethylenediamine and of sodium aminoethoxide in anhydrous ethylenediamine were tested for this purpose. Thiols up to C_{10} dissolve easily in the aqueous solutions, where the anhydrous reagent will dissolve readily every thiol tested (including the difficultly reacting *tert*-hexadecyl mercaptan), except 1-octadecanethiol and high concentrations of 1-hexadecanethiol. Both of these readily react but yield salts only slightly soluble at room temperature which dissolve on warming.

Efficiency of Thiol Extraction. A test procedure was designed for evaluating the efficiency of extraction with various thiols using 1.1*N* sodium aminoethoxide in anhydrous ethylenediamine. One milliliter of thiol dissolved in 25 ml. of isopentane is extracted with 50-ml. and 10-ml. portions of the reagent. Dissolved and entrained isopentane is removed from the extract by reducing the pressure with a water pump.

Table I. Efficiency of Thiol Extraction

Thiol	Recovery, %	Residue, %
Cyclohexanethiol	95	5
1-Octanethiol	95	
2-Octanethiol	98	
tert-Octyl mercaptan[a]	90	2
1-Decanethiol	90	2
1-Dodecanethiol	85	3
tert-Dodecyl mercaptan[a]	96	2
tert-Tetradecyl mercaptan[a]	85	3
1-Hexadecanethiol	80	Solid
tert-Hexadecyl mercaptan[a]	70	20
tert-Hexadecyl mercaptan[a]	95	3

[a] Structure not known.

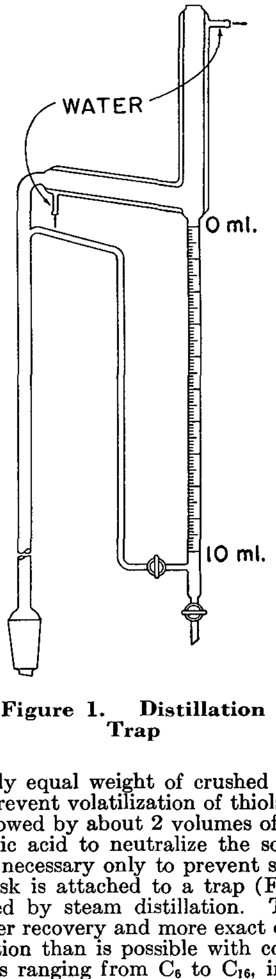
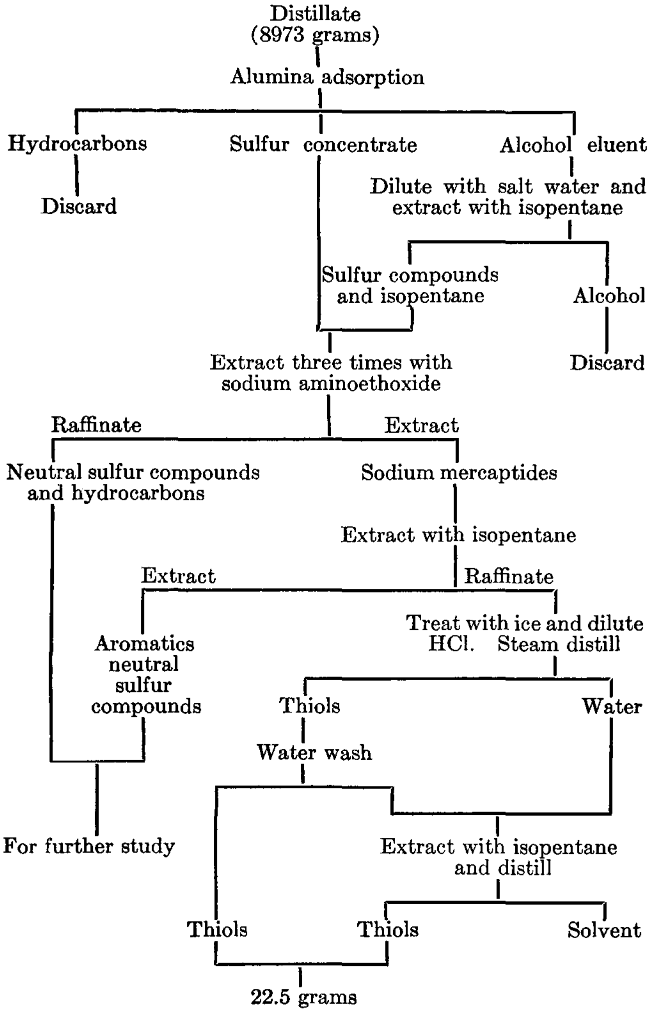


Figure 1. Distillation Trap

An approximately equal weight of crushed ice is then added to the extract to prevent volatilization of thiols from the heat of the hydration, followed by about 2 volumes of water containing enough hydrochloric acid to neutralize the sodium salts. The addition of acid is necessary only to prevent severe corrosion of the flask. The flask is attached to a trap (Figure 1), and the thiols are separated by steam distillation. The trap was designed to give better recovery and more exact observation of the end of the distillation than is possible with conventional traps.

A series of thiols ranging from C_6 to C_{16}, including primary, secondary, and tertiary members, was tested by this procedure, with the results shown in Table I. Commercial materials were used in most cases without purification. In several instances where yields were lowered appreciably by impurities, the isopentane was washed and evaporated and the residue measured. Tests for thiols in the residue were negative in every case.

Table II. Treatment of 111° to 150° C. Boiling-Range Wasson Distillate to Obtain Thiol Concentrate



Thiols containing 16 carbon atoms seem to be the upper limit of usefulness for the distillation method of recovery. Several hours of refluxing were required in this boiling range, and in the case of 1-hexadecanethiol some oxidation to disulfide probably occurred during this time as indicated by a solid residue in the flask after completion of the distillation and cooling. For the lower members of the series, the steam distillation required only a few minutes of boiling.

Sulfide Interference. Similar tests were made on a mixture of a thiol and an alkyl sulfide to determine whether appreciable amounts of sulfides are extracted along with the thiols. When a mixture of 1 ml. of 1-octanethiol and 1 ml. of 5-thianonane in 25 ml. of isopentane was extracted in the manner described, the extract yielded 1.21 ml. of distillate. The extraction was repeated and the extract washed with 50-ml. and 25-ml. portions of isopentane before distillation. The extract yielded 0.95 ml., and 1.00 ml. of residue was obtained by distillation of the isopentane. The purity of the extract as determined by silver nitrate titration was 98%. A similar test with 1-dodecanethiol and 7-thiatridecane yielded 0.87 ml. (87%) of thiol similarly determined to be 99% pure.

PROCEDURE

Preliminary. In applying the method to extraction of distillates two variations in procedure were investigated on two parts of a distillate. One part was passed through activated alumina to concentrate the sulfur compounds, while the other wax extracted directly without any previous treatment. The yields by both methods were essentially equal, but treatment of the whole distillate not only required handling much larger batches of material but also resulted in the accumulation of some aromatic hydrocarbons in the extract, and several back-extractions with isopentane were required to remove them. The concentration process requires the time-consuming and expensive adsorption operation, but this is still necessary for subsequent steps in the separation scheme. About 8 ml. of material resulting from these extractions was distilled in a semimicro column. Cyclohexanethiol was identified by infrared spectroscopy, and subsequent spectral data have shown that a plateau on the distillation curve was caused by substantial amounts of 2-hexanethiol.

Large Scale. The above procedure (Table II) was used on a more comprehensive study of the sulfur compounds in Wasson crude oil boiling between 111° and 150° C. The distillate, which weighed 8973 grams (11.7 l.), was first passed through activated alumina to concentrate the sulfur compounds. This yielded about 500 grams of material. However, some of the sulfur compounds were dissolved in the alcohol used for desorbing the alumina columns. This material was recovered by diluting the alcohol with salt water and extracting the mixture with about 2.5 liters of isopentane.

The main sulfur-containing fraction was then added to the isopentane extract from the alcohol, and this mixture was extracted twice with 125 ml. and once with 100 ml. of 1.9N sodium aminoethoxide in anhydrous ethylenediamine. The three extracts were combined and extracted four times with 50 ml. of isopentane to remove aromatic hydrocarbons and neutral sulfur compounds dissolved or entrained in the extract. Distillation of the isopentane after washing free of amines yielded 3.5 ml., which was predominantly aromatic hydrocarbons. This was returned to the raffinate from the sodium aminoethoxide extraction.

The extract was diluted with about 500 grams of crushed ice, followed by 78 ml. of concentrated hydrochloric acid in 500 ml. of water in a 2-liter boiling flask. A trap was connected to the flask and the mixture refluxed until no more oil separated from the distillate. The regenerated thiols were drawn from the trap, and an additional 200 ml. of water was distilled over to complete volatilization of the thiols. The thiol distillate was washed to remove small amounts of ethylenediamine. The washings were combined with the distillate water and extracted with isopentane, which was then distilled off. The thiols recovered from the washings were combined with the main portion, and the total recovered amounted to 22.2 grams of thiols.

CONCLUSION

After the raffinate was washed and the isopentane distilled, it was discovered that the raffinate still contained traces of thiols. The sample was again extracted with sodium aminoethoxide and yielded an additional 0.3 gram of thiols (total yield 22.5 grams). Analysis of the extract for aromatic hydrocarbons by ultraviolet absorption showed the presence of not more than 0.5%.

It has been determined that 2N sodium aminoethoxide in anhydrous ethylenediamine is an effective reagent for removing thiols from petroleum distillates. The data indicate that the procedure, for practical purposes, is quantitative. Aromatics and other materials, which are somewhat soluble in the reagent, can be removed by washing the extract with isopentane. The thiols are quantitatively recovered by acidifying the sodium salts and steam-distilling the mixture. Ethylenediamine present in the recovered thiols may be washed out with water. Although "whole" distillates can be treated in this manner, it is preferable to concentrate the thiols by adsorption on alumina before extraction to avoid handling excessive quantities of material.

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New Techniques for Adding Organic Acids to Silicic Acid Columns

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In chromatographic separation of organic acids on columns of silicic acid, it has been customary to introduce the sample in an organic solvent to avoid any disruption of the equilibrium between phases. A method is described for successfully adding the organic acids or their sodium salts in the aqueous phase, a procedure which facilitates the quantitative introduction of the acids into the column and eliminates any difficulties from dehydration of the silicic acid. The acids or their salts also may be introduced as a uniform, narrow band by adding them in blotter disks. The techniques should be applicable to all water-soluble organic and inorganic compounds separable on columns of silicic acid.

IN CURRENT techniques for chromatographic separation of free organic acids on silicic acid columns, the sample is usually introduced in the nonaqueous phase. Bulen *et al.* (*1*) employed, as a modification, the mixing of an aqueous acidified solution of organic acids with silicic acid and the addition of this to the top of the column.

It has been considered that the introduction of a sample in aqueous solution results in a water-logged silicic acid column, disrupts completely the equilibrium between the aqueous and nonaqueous phases, and thus prevents any separation of organic acids. This belief, which is probably based on previous unsuccessful attempts to introduce the sample in this manner, is incorrect, and in this investigation methods were developed for overcoming these difficulties and obtaining good separation.

REAGENTS

Technical grade n-butyl alcohol (W. H. Barber Co., Chicago) and chloroform (Merck) were used without redistillation. Mallinckrodt's analytical reagent 100-mesh silicic acid (batch ZVV-I) was used; the fine particles were removed from the silicic acid by repeated suspension in distilled water and decantation. The silicic acid then was dried overnight at 110° C.

EXPERIMENTAL PROCEDURE

Preparation of Column. To avoid a water-logged column an undersaturated column is prepared, although a water level approaching saturation is used to improve the resolution of the organic acids. A silicic acid holding a maximum of 0.8 ml. of water per gram can be used successfully when 0.6 ml. of water per gram is added initially and not over 0.15 ml. of aqueous sample is added subsequently (usually much smaller volumes of sample can be employed). Good separation is achieved when complete hydration of the silicic acid does not extend below the top half of the column.

Four grams of silicic acid mixed with 2.4 ml. of 0.5N sulfuric acid (referred to as the aqueous phase) was made into a slurry with the nonaqueous solvent and was added to a 10-mm. (inside diameter) glass column provided with a sealed-in porous disk. The length of the silicic acid bed was 11.5 to 11.6 cm. Two pounds' pressure was used for packing the column and 1.5 pounds for developing the column. The temperature of operation ranged from 25° to 27° C., and each separation required approximately 1 hour. Two milliliter fractions of developing solvent were collected. The developing solvent contained 35 volumes on n-butyl alcohol to 65 volumes of chloroform. Four volumes of the solvent mixture was equilibrated with 1 volume of 0.5N sulfuric acid. The nonaqueous solvent used for introducing acids in comparative tests consisted of a mixture of equal volumes of chloroform and 2,2-dimethyl-1-propanol (*tert*-amyl alcohol) (*2*).

Introduction of Free Organic Acids in Aqueous Phase into Column. Commonly, the sample of organic acids has been introduced in a solvent miscible with the nonaqueous solvent used in slurrying and developing the silicic acid column (*2*), and no special difficulties have been encountered. In this procedure it is necessary to follow exactly the described technical details. Two immiscible solvents are used—i.e., butyl alcohol–chloroform and water, and in no case should these immiscible solvents be present together on the top of the column. Small drops of butyl alcohol–chloroform remaining on the top of the column will prevent even introduction of the water, so it is important that the top and the sides of the column should be absolutely free of this solvent.

To introduce an aqueous sample, place a blotter disk (with a diameter 0.2 to 0.3 mm. greater than that of the column) on the top of the column while a 3-cm. depth of solvent is still present. (A light gray blotting paper without embossed pattern, 140-pound stock, obtained from the Wrenn Paper Co., Middleton, Ohio, has proved satisfactory; other highly porous blotters will doubtless serve. The disks should be cut accurately with clean edges, and this is best done with a frequently sharpened cork borer turned by a drill press.)

Press the blotter disk on the top of the column with a glass tube whose outside diameter is nearly the same as the inside diameter of the column; inside the tube should be a cork, flush with the bottom, which has a 1-mm. central hole. All air bubbles are removed when the blotter disk is pressed into position. Close off the bottom of the column with a pinch clamp, and wait approximately 1 minute. Pour out or pipet off the excess solvent from the top of the column, and remove any residual solvent with a bacteriological inoculating needle carrying a plug of absorbent cotton. The top of the blotter disk should still be moist. The handle of the inoculating needle should be split and should have a narrow strip of qualitative filter paper twisted around the handle and then bent back on itself; wipe drops of solvent from the walls of the column with this paper.

To add the sample, introduce the pipet into the column, without touching the walls, to a distance about 2 mm. above the middle of the blotter disk. Open and close the pinch clamp quickly to draw any excess butyl alcohol–chloroform away from the upper surface of the blotter disk; at the same time be careful not to admit any air into the blotter disk. (If the blotter disk is not drained sufficiently, drops of butyl alcohol–chloroform may appear on top of the disk.) Now immediately introduce all of the sample, covering the blotter disk evenly with aqueous phase. While the pinch clamp is still closed, the undersaturated column starts to absorb the sample.

Rapidly open and close the pinch clamp to allow controlled addition of the sample into the column and to avoid overrunning

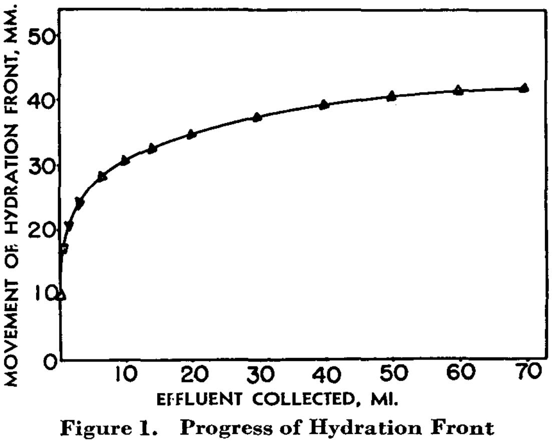

Figure 1. Progress of Hydration Front

0.5 Ml. of aqueous sample was added to a 10-mm. diameter 4-gram column of silicic acid with accompanying introduction of air. Wash the sample in with developing solvent according to the standard procedure described by Isherwood (*2*), and develop the column as he describes. With a little practice, an even introduction of an aqueous sample can be achieved.

The aqueous sample will saturate the upper portion of the column and produce a white horizontal band; the developing solvent will carry excess water into the lower, unsaturated part of the column. The hydration of the column is rapid in the first stages of development, but progresses slowly during the rest of the run (Figure 1). If too much aqueous phase is added, the excess will pass completely through the column, and the sulfuric acid in this aqueous fraction will be titrated together with the last organic acids eluted from the column. When the hydration of the column is controlled by proper introduction of the sample, a separation of acids as shown in Figure 2 is achieved.

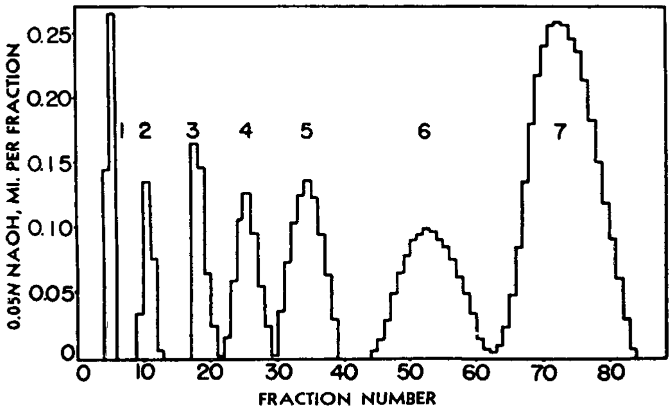

Figure 2. Separation of Organic Acids (25 Mg. of Total Acids) Introduced in Free Form in 0.5 Ml. of Aqueous Phase on 10-Mm. Diameter 4-Gram Column of Silicic Acid

Fractions 1 to 9, 1.0 ml.; 10 to 63, 2.0 ml.; 64–84, 2.25 ml.
Acid peaks. 1, propionic; 2, succinic; 3, oxalic; 4, glycolic; 5, malic; 6, citric; 7, isocitric

Introduction of Sodium Salts of Organic Acids in Aqueous Phase. The treatment of the column before adding the sample is the same as described for the separation of free acids. Sodium salts of nonvolatile acids can be acidified before placing the solution on the column, and the method described in the preceding section then can be followed. The sodium salts of volatile acids should be acidified directly on the top of the column in the following way:

Add 1 drop of phenol red indicator to the solution of sodium salts. Proceed in the previously described manner, but before introducing the sample add 0.2 ml. of 9*N* sulfuric acid (saturated with developing solvent) to the top of the column. Follow this immediately with the aqueous solution of sodium salts and then with 0.1 ml. of 9*N* sulfuric acid.

When the color change from red to yellow to orange-red occurs, it will indicate that the organic acids are liberated from their salts (pH below 1.0). Open the pinch clamp and allow the mixture to soak quickly into the column. When the aqueous phase is all in the column, then develop as described by Isherwood (*2*).

Introduction of Free Nonvolatile Organic Acids in Blotter Disks. The sample is placed on the column without solvent. Cut a disk of even thickness having the same diameter as the inside of the column from a 1-mm. thick white porous blotter. Thread a 22-gage Nichrome wire, sharpened at one end and flattened like a pin head at the other, through the center of the disk. Add 0.5 ml. of the solution of free organic acids (25 mg. of acids) containing 1 drop of phenol red indicator to the disk by alternately allowing a few drops to soak into each side of the disk, and drying it under an infrared lamp.

Remove the wire, and place the dry disk on the column upon which a 1-mm. layer of solvent still remains. Push the disk down with the glass tubing and cork device described for addition of the blotter disk until it is 1 to 2 mm. above the solvent; then push it down evenly with a pointed inoculating needle. Release the pinch clamp at the base of the column and wash the organic acids from the disk into the column by slow dropwise addition of the developing solvent (total volume about 0.2 ml. for a 1-cm. diameter column). Follow this by washing with three 0.1-ml. portions of solvent.

Even and quick removal of the indicator from the disk will show that the size of the disk was suitable and the preparation of the sample was correctly performed. Good separation is obtained because the sample is dispersed inside the disk very evenly; such even dispersal is difficult to achieve by introducing the sample as a powder or as crystals. When no convenient solvent can be found in which to introduce the sample into the column, this method allows direct addition of the sample in a concentrated and yet evenly dispersed form. An example of a separation of free organic acids added in a blotter disk is shown in Figure 3.

Introduction of Sodium Salts of Volatile or Nonvolatile Acids in Filter Paper Disks. Suspend qualitative filter paper in a saturated solution of sodium bicarbonate with a Waring Blendor and compress the heavy suspension in a hydraulic press to a thickness of 2 mm. Dry the pad in the oven at approximately 40° to 50° C., and cut disks of a suitable diameter with a cork-borer as described.

Introduce sodium salts of organic acids into these disks as described. Place 0.1 ml. of 9*N* sulfuric acid above the column and immediately add the disk; while 1 mm. of acid still remains above the column add another 0.1 ml. of 9*N* sulfuric acid. Escaping carbon dioxide expands the disk sufficiently to allow quick and even access of sulfuric acid into the disk. No detectable carbonic acid passes through the column.

DISCUSSION OF RESULTS

When organic solvents have been used for sample introduction, it has been accepted that they should be added in minimum volume. When the sample is added in a polar nonaqueous solvent, an increased amount of this solvent increases the R_f values of organic acids and simultaneously broadens the base of the acid peaks; both these effects harm good resolution.

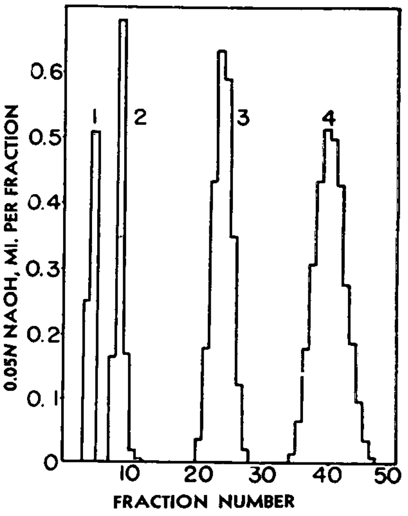

Figure 3. Separation of Organic Acids (25 Mg. of Total Acids) Introduced in Free Form on Disk of Blotting Paper

Two milliliter fractions collected from 10-mm. diameter 4-gram column of silicic acid
Acid peaks. 1, succinic; 2, oxalic; 3, malic; 4, citric

Several quantitative experiments were performed to determine the effect of the amount of the aqueous sample on the separation of organic acids. The resolving power of columns to which aqueous samples were added was superior to that of similar columns receiving samples in *tert*-amyl alcohol–chloroform, and no increase in R_f values was observed with increasing amounts of water. With increasing water the bases of the peaks were broadened, and the limit of aqueous phase which can be added was indicated by this broadening of the peaks of the slowest moving acids. The best results were obtained when the column was prepared with the maximum amount of water (consistent with the previously discussed criteria) and the aqueous sample was introduced in a minimum volume.

With the silicic acid employed, 15 to 30 mg. of organic acids can be separated very effectively on a 10-mm. diameter column containing 4 grams of silicic acid. Emergence of the acids (as in Figure 2) is reproducible to a single tube if care is employed in adhering to standard operating conditions. The recovery from the column of added known acids is 90 to 100%.

Advantages of Introducing Sample in Water Phase. The new technique for the introduction of samples in the water phase constitutes a simplification of the generally used methods. It eliminates the tedious and often nonquantitative transfer of the sample from the aqueous to the nonaqueous phase (*2*). As the sample is introduced in the water phase, acidification of the sodium salts directly on the column becomes possible, and the loss of volatile acids is decreased appreciably. The method permits the separation of compounds, such as glyoxylic acid which tend to form hydrates and are not readily extractable by organic solvents.

Direct addition of the sample to the column in the aqueous phase should be useful in the routine and exploratory separation of organic acids from such aqueous biological materials as fermentation media, vegetable and fruit juices, plant saps, and deproteinized extracts from animal tissues. This chromatographic technique has been used for the separation of organic acids, but it may be applied *generally to water-soluble organic and inorganic compounds*.

The new procedure gives at least as good separation and recovery of organic acids as is obtained when the acids are introduced in an organic solvent. Dehydration of the column, which is often troublesome with samples added in an organic solvent, is eliminated in this method. The only apparent disadvantage in the use of the method described is that skill must be developed in the addition of the samples.

Advantages of Introducing Sample on a Paper Disk. Introduction of the sodium salts of organic acids on paper disks followed by acidification has essentially the same advantages as those cited for the introduction of sodium salts in the aqueous phase. Free organic acids introduced as solids in paper disks are separated better than when they are introduced in the aqueous or organic phase. Compounds soluble only in a large amount of organic solvent can be concentrated in a paper disk, and this decrease in sample volume improves their separation.

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Determination of Oxygen in Sodium

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A method for the determination of sodium monoxide in sodium depends upon the reaction between sodium and excess *n*-butyl bromide (1-bromobutane) in hexane solution. Sodium monoxide does not react with the reagent and can be determined, after the addition of water, by titration. Both oxygen and other impurities can be determined on the same sample, and the method requires only the simplest equipment and is easily adaptable to the analysis of large numbers of samples. The standard deviation is 0.003 to 0.005%. The method has been applied to sodium that has been sampled in glass and in metallic containers. It is believed that the method will be applicable in the range 0 to 0.02%, if large samples are used.

THE oxygen content of sodium is of interest because of the extreme reactivity of sodium monoxide at elevated temperatures. The oxide reacts with all the common metals (including the platinum group metals), graphite, and ceramic materials, and because of this extreme reactivity, other impurities besides oxygen are often determined in sodium. Ideally, determinations of both oxygen and impurities should be made on the same sample, thus providing a sounder interpretation of data as well as economy of sample. This investigation was undertaken for the specific purpose of determining oxygen and other impurities on the sample of sodium.

A method which has been previously developed for this determination is that of Pepkowitz and Judd (*4*). Essentially, this method depends upon the extraction of sodium with mercury in an inert atmosphere and the separation of the residual sodium monoxide, which is insoluble in mercury. With this method, however, it is not practicable to determine oxygen and impurities on the same sample. A modification of the Pepkowitz and Judd method has been reported by Williams and Miller (*6*).

A new method has been developed which is based upon the fact that *n*-butyl bromide (1-bromobutane) reacts with sodium to form the neutral salt, sodium bromide, but does not react with sodium monoxide. Following this reaction, dissolution of the residue in water yields titratable sodium hydroxide (from the monoxide) in a solution of sodium bromide. The development of this method has, accordingly, entailed a study of the reaction of *n*-butyl bromide with sodium and with sodium monoxide.

REACTION OF *n*-BUTYL BROMIDE WITH SODIUM

In the Wurtz synthesis of hydrocarbons (*1*), an excess of sodium is present. A series of tests was conducted to determine whether the reaction proceeds to completion when an excess of the alkyl halide is present. Small amounts of sodium were added to large excesses of propyl, butyl, and amyl chlorides, bromides, and iodides (chloro-, bromo- and iodo-propanes, butanes, and pentanes).

$$2\mathrm{Na} + \mathrm{RX} \rightarrow \mathrm{RNa} + \mathrm{NaX} \qquad (1)$$
$$\mathrm{RNa} + \mathrm{RX} \rightarrow \mathrm{NaX} + \mathrm{R\text{-}R} \qquad (2)$$

In all cases sodium was converted to the halide with explosive violence. The rate of reaction varied little with the halide used.

Diluents in the form of hydrocarbons, which are inert to sodium, were added to the halides in order to decrease the reaction rate. Hydrocarbons with boiling points higher than that of

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the halide had little effect, even in a solution of 90% hydrocarbon by volume. Hydrocarbons with boiling points lower than that of the halide reduced the reaction rate to controllable limits. The role of the hydrocarbon in the reduction of the reaction rate is evidently that of a heat transfer agent. Dissipation of heat must be rapid enough to prevent the halide from reaching such a temperature that an explosive reaction with sodium occurs. In this regard, *n*-hexane, boiling point 67° to 71° C., proved particularly effective.

Of the various halides cited, *n*-butyl bromide, boiling point 101.6° C., was most satisfactory. A solution of 40 to 60 volume % *n*-butyl bromide in hexane reacts suitably with 0.1 to 20 grams of sodium. When the bromide concentration is increased to 80 volume %, the hexane is volatilized during the reaction, which then becomes uncontrollable. Concentrations much lower than 20 volume % react too slowly.

A five- to sevenfold excess is optimum for less than 5 grams of sodium. For larger samples a threefold excess is recommended. In general, when the quantity of bromide is appreciably less than optimum, the time for complete reaction is of the order of 10 to 15 hours. Greater excesses offer little advantage.

REACTION OF *n*-BUTYL BROMIDE WITH SODIUM MONOXIDE

Literature sources yield little information on the reaction of *n*-butyl bromide with sodium monoxide, but it was postulated that the following reactions were possible:

$$Na_2O + C_4H_9Br \rightarrow C_4H_9ONa + NaBr \quad (3)$$

$$C_4H_9ONa + C_4H_9Br \rightarrow C_4H_9OC_4H_9 + NaBr \quad (4)$$

Equation 4 represents the Williamson synthesis of ethers (*2*). In the proposed method, following the reaction of sodium with the halide, the residue of sodium bromide and other products is dissolved in water, and from the alkali formed the monoxide content is calculated. The formation of any organic compound which yields an equivalent amount of hydroxide upon hydrolysis will not affect the results.

$$Na_2O + H_2O \rightarrow 2NaOH \quad (5)$$

$$C_4H_9ONa + H_2O \rightarrow NaOH + C_4H_9OH \quad (6)$$

$$C_4H_9OC_4H_9 + H_2O \rightarrow \text{no reaction} \quad (7)$$

No oxygen is lost in Equation 6, since it can be recovered by hydrolysis and an alkalimetric titration. A loss of oxygen would occur, however, if dibutyl ether, which is not hydrolyzed by water, were formed.

To determine the extent of ether formation 10 to 50 mg. of sodium monoxide was placed in a solution of 50% *n*-butyl bromide in hexane and allowed to stand for various periods of time at 60° to 65° C. The conditions of the test were selected to approximate those under which the reaction with sodium is conducted. The residual sodium monoxide, which was visibly unchanged even after 72 hours' contact, was filtered and dissolved in water, and the sodium hydroxide formed was titrated. The results of these tests are shown in Table I.

The precision was not so high as might be desired because of the difficulties encountered in the handling of sodium monoxide. The monoxide was weighed by difference and kept over phosphorus pentoxide. The reagent when received was 97.5% sodium monoxide and 2.5% sodium peroxide. To eliminate the effect of possible changes in the oxide upon standing, total basicity determinations were carried out simultaneously with the butyl bromide tests.

The results indicated no formation of dibutyl ether after 36 hours. In only isolated cases was the quantity of base found less than that which was added. In all tests when the contact time exceeded 24 hours, the base found was less than that added, although the losses were slight and can hardly be considered significant under the conditions of the tests. No dibutyl ether could be detected in the filtrate.

The possible loss of basicity in the filtrate was checked by titrating the hydrolyzed filtrate. In no case was any basicity found, even for the trials of 72 hours' contact. It seems evident that no soluble alcoholate is formed under these conditions. It may be concluded from these tests that sodium monoxide and 50% *n*-butyl bromide in hexane do not react over a period of at least 24 hours.

Table I. Recovery of Sodium Monoxide after Contact with *n*-Butyl Bromide

Contact Time, Hours	Sodium Monoxide, Mg. Added (*A*)	Found (*B*)	Difference (*B* − *A*)	Recovery, %
2	13.2	14.0	0.8	106
	17.5	17.0	−0.5	97
16	20.9	20.7	−0.2	99
	25.0	25.9	0.9	103
	48.9	49.0	0.1	100
24	19.6	19.8	0.2	99
	52.6	52.2	−0.4	99
36	22.2	22.0	−0.2	99
	21.5	21.3	−0.2	99
	27.2	26.5	−0.7	97
72	20.7	20.3	−0.4	98
	34.0	33.4	−0.6	98
	27.1	26.5	−0.7	98
	13.3	11.4	−1.9	86

PROCEDURE

Purification of Reagents. *n*-Butyl bromide is purified by washing the commercial grade material with concentrated sulfuric acid until the acid layer was clear to remove unsaturated compounds. The residual sulfuric acid in the reagent is neutralized with sodium bicarbonate, and the reagent is subjected to a preliminary drying with calcium chloride. It is then distilled and stored in a dark bottle in an argon atmosphere in contact with activated alumina. *n*-Butyl bromide treated in this manner remained sufficiently dry and free of oxygen for use in the determination for several weeks.

Hexane is treated by drying over sodium ribbons, distilling from this medium, and storing in a dark bottle over sodium. In order to prevent possible oxygen contamination, an atmosphere of oxygen-free argon should be maintained in the hexane container. Some lots of hexane were observed to discolor the sodium upon long standing. Hexane which had been washed with sulfuric acid could be stored for several weeks without evidence of change.

The quantity of water in the purified and dried reagents was less than 2 p.p.m. as determined by the Karl Fischer (*3*) method.

Samples Sealed in Glass. A sealed sample normally containing 1 to 2 grams of sodium, is placed in a 4 × 20 cm. tube, with a reinforced bottom, containing 100 ml. of a solution of 50 volume % *n*-butyl bromide in *n*-hexane. If the sample size is 15 to 20 grams, the reagent volume and tube size should be increased accordingly. The glass tube is crushed by means of a heavy glass rod (10-mm. diameter), flattened at one end. As the reaction proceeds, the glass rod is used to continually expose fresh sodium to the reagent.

The tube is placed in a sand bath, which is maintained at 60° to 70° C., to complete the reaction which requires 1 to 2 hours. Care should be taken to prevent excessive boiling of the solution which volatilizes hexane from solution. The reaction of 2 grams of sodium will generate enough heat to obviate long periods of external heating. The reaction may be allowed to stand overnight without adverse effects if an inert-gas blanket is maintained over the tubes.

The residue is cooled and powdered to ensure the complete reaction of small particles of sodium, and 100 to 200 ml. of water free of carbon dioxide is added to dissolve the residue and to form a two-phase system: the aqueous phase, which is a solution of sodium bromide and sodium hydroxide, and the organic phase, which consists of excess reagent and the newly formed octane. The phases are separated in a separatory funnel and the water phase is titrated to pH 7 with 0.001*N* nitric acid using a glass electrode, which responds in solutions of high sodium ion concentration. This volume of titrant is used to calculate the oxygen content.

$$\text{Acid, meq.} \times 0.008 = \text{oxygen, grams}$$

The neutralized solution is diluted to 500 ml., and a 25-ml. aliquot is titrated with 0.5*N* silver nitrate using eosin as the indicator. The sample weight of sodium is calculated as follows:

$$\text{Silver nitrate, meq.} \times 0.023 = \text{sodium, grams}$$

Table II. Oxygen Content of Double-Distilled Sodium

Group	Sodium, Grams	Oxygen Mg.	Oxygen %
A	2.103	1.12	0.053
	2.212	1.15	0.052
B	1.362	0.344	0.025
	1.340	0.420	0.031
	0.946	0.166	0.018
	0.323	0.327	0.025
	0.895	0.188	0.021

Standard deviation = 0.004

Table III. Recovery of Known Amounts of Oxygen in Sodium[a]

Oxygen, % Added	Oxygen, % Blank[b]	Oxygen, % Total (blank + added)	Found	Difference
0.224	0.054	0.278	0.285	+0.007
0.101	0.054	0.155	0.158	+0.003
0.110	0.054	0.164	0.161	−0.003
0.218	0.054	0.272	0.282	+0.010
0.145	0.054	0.199	0.210	+0.011
			Average	0.007

[a] Oxygen added as sodium peroxide.

[b] Average of three determinations.

This weight is high by the amount of sodium in the sodium hydroxide formed. However, as this error is insignificant, it may be disregarded in practically all cases. No holdup of sodium in the organic phase was noted.

The remainder of the aqueous solution and the organic layer are available for the determination of metallic impurities.

Samples Sealed in Metal Containers. Metallic containers of sodium are treated by melting the contents in *n*-nonane or 2,2,5-trimethylheptane. These liquids do not react with sodium or sodium monoxide, and have boiling points higher than the melting point of sodium and densities lower than that of sodium.

The sample is opened under mineral oil and transferred to the reaction tube containing 50 to 75 ml. of nonane. The tube is heated slightly above 100° C. while covered with dry argon and the sodium melted from the tube. *n*-Nonane must be removed before the halide solution is added. This is accomplished by successive dilution with hexane and withdrawal of the mixture. The remainder of the procedure is as described previously.

RESULTS

The range of oxygen concentration extended from 0.001 to 0.1%. In an attempt to obtain sodium with an oxygen content in the lower part of this range, the metal was double-distilled under high vacuum. Published results for oxygen in sodium prepared in this manner vary somewhat, the general average being about 0.02%. The results of determinations of these samples are given in Table II.

Standard samples containing larger amounts of oxygen were prepared by adding known quantities of high purity sodium peroxide to sodium at 300° to 400° C. to form sodium monoxide quantitatively.

$$Na_2O_2 + 2Na = 2Na_2O \qquad (8)$$

This reaction proceeds with considerable violence if the temperature is increased rapidly; however, with the use of a sand bath for heating and a high ratio of sodium to sodium peroxide (approximately 100 to 1) a smooth reaction occurred. Mineral oil, previously conditioned by heating under argon to 400° C. in contact with sodium, was used as inert medium for the reaction. Typical results are shown in Table III.

A further evaluation of the method has been made on the basis of the results of 31 duplicate determinations, the results of which are shown in Table IV. These samples were contained in two-bulb glass sample tubes which were filled by drawing molten sodium into the tubes. The designations "upper" and "lower" refer to the position of the bulbs during filling; the sodium entered the tube, passed through the lower bulb and on into the upper bulb. The two bulbs were then separated to provide duplicate samples.

Table IV. Duplicate Determinations of Oxygen in Sodium

Sample	Oxygen, % Upper bulb (A)	Oxygen, % Lower bulb (B)	Difference ($A - B$)
1	0.022	0.020	0.002
2	0.024	0.023	0.001
	0.023	0.025	−0.002
3	0.024	0.026	−0.002
4	0.027	0.025	0.002
5	0.025	0.027	−0.002
6	0.024	0.030	−0.006
7	0.028	0.027	0.001
8	0.029	0.029	0.000
9	0.029	0.029	0.000
10	0.027	0.031	−0.004
11	0.026	0.033	−0.007
12	0.030	0.030	0.000
13	0.030	0.030	0.000
14	0.029	0.032	−0.003
15	0.030	0.031	−0.001
16	0.032	0.029	0.003
17	0.035	0.030	0.005
18	0.032	0.036	−0.004
19	0.034	0.034	0.000
20	0.035	0.034	0.001
21	0.035	0.038	−0.003
22	0.038	0.043	−0.005
23	0.047	0.039	0.008
24	0.051	0.039	0.011
25	0.053	0.052	0.001
26	0.055	0.054	0.001
27	0.052	0.064	−0.012
28	0.063	0.057	0.006
	0.052	0.061	−0.009
	0.059	0.052	0.007
		Algebraic sum	−0.012
		Average difference	0.003

Number of cases in which $A > B$ = 13
Number of cases in which $A < B$ = 13

Standard deviation.
Calculated from average range −0.0030
Calculated from sum of variance −0.0034

DISCUSSION

The oxygen values are all higher than usually found for carefully distilled and handled sodium. The samples were possibly contaminated by sodium hydroxide and sodium carbonate. As neither of these reacts with *n*-butyl bromide, they would be included in the titration step as oxygen.

The recovery of oxygen added as sodium peroxide provides a check on the method at higher concentrations of oxygen. In general, such high values would rarely be encountered in high grade sodium. The average difference of 0.007% is satisfactory under such conditions.

A comparison of the results obtained on identical samples by the Pepkowitz and Judd method shows an average difference of 0.008%, and in only a few cases a difference greater than 0.01%. In general, there is no indication that one method tends to yield higher or lower results than the other.

The standard deviation for the results of duplicate determinations listed in Table IV is 0.0034%. The precision in this case was better than for any of the other results reported. The probable explanation is that the precision of the method is actually as good as is indicated and that the poorer precision observed for the other tests is a result of sample heterogenity. However, the duplicate determinations listed in Table IV were made at the same time, side by side; such a procedure often effects an improvement, which is actually fictitious, in the apparent precision of a method. It is evident from the data in Table IV that there was no consistent tendency toward segregation; both upper and lower sample bulbs contained, on the average, the same quantity of oxide.

The standard deviation of the present method is in the range 0.003 to 0.005% which compares favorably with that for the Pepkowitz and Judd method. Modifications in the amalgamation procedure by Pepkowitz, Judd, and Downer (*5*) have led to increased precision of the order of 0.0016%.

The present method is satisfactory for samples of sodium containing more than 0.02% oxygen. Because of the lack of samples of suitably low oxygen content, the method has not been sufficiently investigated with respect to lower ranges of oxygen concentration. Samples as large as 20 grams have been handled by this method, indicating the wide range of sample size which can be tolerated. Such large-sized samples are not practical for routine analytical use because of the volume of reagents required and excessive reaction time.

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Gravimetric Determination of Tetramethylphosphonium Ion

Use of Chloroplatinic Acid as Precipitant

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A need arose for the determination of the tetramethylphosphonium ion. As the ion behaved like the potassium ion, this resulted in the development of a method of analysis based on the formation of an insoluble chloroplatinate which can be weighed. When pure materials are used, the method has an accuracy of better than 99.5% and a precision of 2 parts per thousand. An ion exchange method has been developed for the separation of tetramethylphosphonium ion from anions using Rohm & Haas IR 100 H cation exchange resin.

IN RECENT years the chemistry of organic phosphorus compounds has become a field of numerous investigations and research. Of particular importance has been the interest in organic onium salts because of the possible application of their biocidal and surface active properties. Kosolapoff (*1*) has compiled most of the literature available on this subject. A search of this and the literature in general yielded no specific method for the analysis of such compounds and in particular tetramethylphosphonium ion (TMP). Because of this, a procedure for its analysis was devised.

The tetramethylphosphonium ion has four phosphorus-to-carbon links which account for its unusual stability. Investigations have shown that it is resistant to oxidation. When its chloride salt (TMPC) was evaporated with a mixture of nitric and perchloric acids to dense white fumes, the resulting solution yielded none of the usual reactions of the orthophosphate ion. Additional experiments showed that the tetramethylphosphonium ion remained unaltered and intact after treatment with nitric and perchloric acids. Phosphine may be distilled from alkaline solutions of phosphonium (PH_4^+) salts; however, all attempts to distill trimethylphosphine from an alkaline solution of tetramethylphosphonium ion failed.

A resemblance between the tetramethylphosphonium ion and both the potassium and the ammonium ions was observed. Many of the reagents (chloroplatinic acid, perchloric acid, 2,2′,4,4′,6,6′-hexanitrodiphenylamine, picric acid, and silicotungstic acid) which precipitate potassium and ammonium ions also precipitate tetramethylphosphonium ion. Because chloroplatinic acid is a common laboratory chemical and is available in a pure state, it was tried first as a quantitative precipitating agent.

CHLOROPLATINATE METHOD

The procedure described has been used successfully in this laboratory for the determination of the tetramethylphosphonium ion for over a year. This method is based on the insolubility of tetramethylphosphonium chloroplatinate, $[(CH_3)_4P)]_2PtCl_6$, in ethyl alcohol. The sample in the chloride form, free from other substances, is treated with an excess of chloroplatinic acid and evaporated to a small volume.

$$(CH_3)_4PCl + H_2PtCl_6 \rightarrow [(CH_3)_4P]_2PtCl_6 + 2HCl$$

The residue is extracted with ethyl alcohol, filtered, and weighed after washing and drying. Ammonium, potassium, rubidium, and cesium ions all form ethyl alcohol–insoluble chloroplatinates, thereby contaminating the precipitate. Moderate amounts of calcium, strontium, and magnesium chlorides can be tolerated.

Because of the cost of the chloroplatinic acid a series of experiments was carried out to determine the optimum ratio of reagent to the chloride salt necessary for quantitative precipitation (Table I). It was found that 0.32 gram of chloroplatinic acid is the minimum quantity of reagent required for a quantitative recovery of 0.2 gram of tetramethylphosphonium chloride. This represents a ratio of 1.6 to 1. The procedure prescribes a 2 to 1 ratio which permits slightly larger samples.

Table I. Ratio of Chloroplatinic Acid to Tetramethylphosphonium Chloride (TMPC)[a]

TMPC				
Added, gram	Recovered, gram	Recovered, %	Ratio of H_2PtCl_6 to TMPC	Ratio of Pt to TMPC
0.1940	0.1008	51.96	0.79	0.38
0.1940	0.1486	76.60	1.18	0.56
0.1940	0.1939	99.95	1.58	0.75
0.1940	0.1944	100.21	1.97	0.94
0.1940	0.1939	99.95	2.36	1.12
0.1940	0.1936	99.79	2.75	1.31

[a] 5-ml. aliquot of standard solution of tetramethylphosphonium chloride used in each case.

Since the mode of evaporation may vary with the operator and thus affect the actual ratio of alcohol to water in the final solution, samples were run using alcohol solutions of varying strength for diluting and subsequent washing (Table II). The results indicate that the evaporation must be carried out so that on cooling a solid mass forms. Failure to do this tends to dilute the alcohol, which increases the solubility of the precipitate.

Table II. Effect of Alcohol Strength on Recovery of Tetramethylphosphonium Chloride (TMPC)

Alcohol, %	TMPC Added, gram	 Recovered, gram	 Recovered, %
95	0.4131	0.4131	100.00
85	0.4131	0.4125	99.85
75	0.4131	0.4103	99.32
65	0.4131	0.4058	98.23

Reagents. Chloroplatinic acid hexahydrate ($H_2PtCl_6.6H_2O$), 10% solution.

Ethyl alcohol, C.P., 95%.

Nitric acid, C.P., concentrated.

Perchloric acid, C.P., 60%.

Hydrochloric acid, C.P., concentrated.

Procedure. Dissolve the sample (about 0.2 gram of tetramethylphosphonium chloride) in 10 ml. of water. If organic matter is present, add 5 ml. of nitric acid and 5 ml. of perchloric acid, observing the usual safety measures for handling perchloric acid (*2*). Evaporate to dryness. Dissolve the perchlorate using a minimum amount of water, and add 0.5 ml. of hydrochloric acid. Add, with stirring, 5 ml. of chloroplatinic acid. Because tetramethylphosphonium chloride is very hygroscopic, care should be exercised in weighing. The precipitation should be carried out in a place free from ammonia fumes, for they will also be precipitated if present. Evaporate the solution to a sirupy consistency, which upon cooling forms a solid mass. The sample should not be evaporated to complete dryness or at too high a temperature. Cool, add 10 ml. of 95% ethyl alcohol, and break up the residue with a stirring rod. Filter the solution through a tared sintered-glass crucible (medium porosity). Wash the residue free of impurities with 95% ethyl alcohol until the filtrate comes through clear. Dry at 120° C. for 1 hour, cool, weigh, and make the following calculations.

Tetramethylphosphonium chloride, grams = 0.4289 × weight of precipitate, grams.

Tetramethylphosphonium ion, grams = 0.3087 × weight of precipitate, grams.

Phosphorus, grams = 0.1050 × weight of precipitate, grams.

Recovery of Platinum (*3*). RESIDUES. Add the residue to about 500 ml. of water. Add a slight excess of formic acid and let stand until the supernatant liquid becomes clear. This usually requires a few days. Filter, and wash with hot water.

FILTRATES. Evaporate the ethyl alcohol and then treat as a residue.

Preparation of Chloroplatinic Acid. Dissolve the platinum in aqua regia and evaporate to a thick sirup. Evaporate alternately with hydrochloric acid and water three times. To convert any chloroplatinous acid to chloroplatinic acid, saturate the warm solution with chlorine gas until it becomes yellow. Evaporate to a sirup to remove the chlorine and dilute to a 10% solution.

Accuracy and Precision. An examination of the results contained in Table III indicates that the error of the method is less than 0.5%. The precision of the method may be judged by the agreement between duplicate determinations on unknown samples. Table IV gives some typical results.

Table III. Recovery of Tetramethylphosphonium Chloride (TMPC)

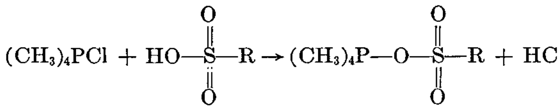
TMPC Added, gram	 Recovered, gram	 Recovered, %	Deviation, %
0.1289	0.1284	99.61	−0.03
0.1788	0.1782	99.66	+0.02
0.1953	0.1942	99.48	−0.16
0.2055	0.2051	99.81	+0.17
		Av. 99.64	±0.10

Table IV. Analysis of Unknowns

First Analysis, %	Second Analysis, %	Difference, %
96.79	96.86	0.07
99.50	99.28	0.22
11.26	11.25	0.01
4.63	4.67	0.04
2.11	2.07	0.04
24.00	23.96	0.04
2.05	2.07	0.02
20.25	20.17	0.08

ION EXCHANGE SEPARATION

Since the tetramethylphosphonium ion is a cation, it can be removed from a solution with cation exchange resins. About 5 ml. of Rohm & Haas cation exchange resin IR 100 H in a 10-ml. buret, using a slow flow rate, proved to be satisfactory for the separation of approximately 0.2 gram of the ion from a neutral water solution of the chloride.



$$(CH_3)_4PCl + HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-R \rightarrow (CH_3)_4P-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-R + HCl$$

The hydrochloric acid liberated in the reaction was titrated quantitatively in the effluent with $0.1N$ sodium hydroxide (Table V). When the column is leached with about 50 ml. of 1 to 1 hydrochloric acid, tetramethylphosphonium chloride is found in the eluate and may be determined by the method described.

Table V. Separation of Tetramethylphosphonium Chloride (TMPC)

TMPC Added, Gram	NaOH Titration of Effluent TMPC, gram	 TMPC, %	H_2PtCl_6 Precipitate after Leaching TMPC, gram	 TMPC, %
0.1939	0.1927	99.38	...	...
0.1939	0.1914	98.71	...	...
0.1939	0.1926	99.33	0.1963	101.1
0.1939	0.1926	99.33	0.1955	100.8

This technique may be extended to the estimation of tetramethylphosphonium ion in the absence of other cations. It would, of course, be necessary to correct for any acidity or basicity initially present in the sample. The use of a cation exchange resin also offers a clean cut method for the gross separation of the ion from anions.

ACKNOWLEDGMENT

The authors wish to express their appreciation to C. A. Wamser for his interest and cooperation in this investigation.

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Potentiometric Differentiation of Certain Inorganic Cations

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Nonaqueous titrations have proved useful for the differentiation of organic bases of varied strength. It was thought feasible to extend such titrations to certain inorganic cations having the common acetate anion. The acetates of ammonium, lithium, potassium, and sodium were titrated potentiometrically as bases in an acetic acid–chloroform solvent. It was possible to differentiate quantitatively between potassium and sodium acetates in the presence of each other. The differential titration of a mixture of inorganic and organic bases under similar experimental conditions was studied.

A NUMBER of investigators have successfully determined inorganic cations, such as sodium, potassium, and lithium, in the presence of each other by various techniques. These methods include flame photometry, spectroscopy, ion exchange chromatography (*1*), and precipitations. Potentiometric titrations in water have not permitted a distinction between these cations.

An excellent review of the theory concerning different systems of acids and bases has been presented by Hall (*2*). Kolthoff and Willman (*3*) have studied the acid strength of inorganic cations and the basic strength of inorganic acetates in acetic acid, using conductometric and colorimetric methods for the determination of the end point.

Investigations in this laboratory have shown (*4*) that many inorganic cations can be titrated with perchloric acid in nonaqueous medium. In the present work, a procedure was developed for determining the relative basicity of the acetates of

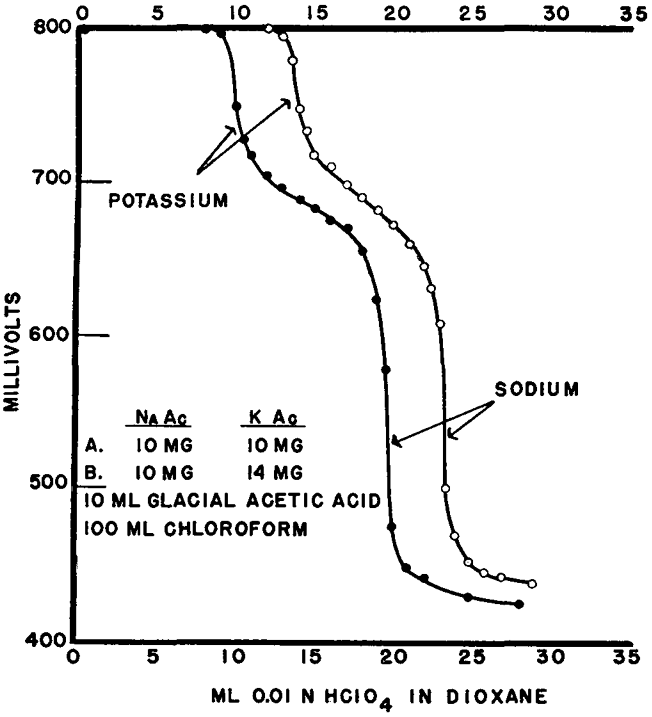

Figure 1. Titration of Sodium and Potassium Acetates

● A curve. ○ B curve

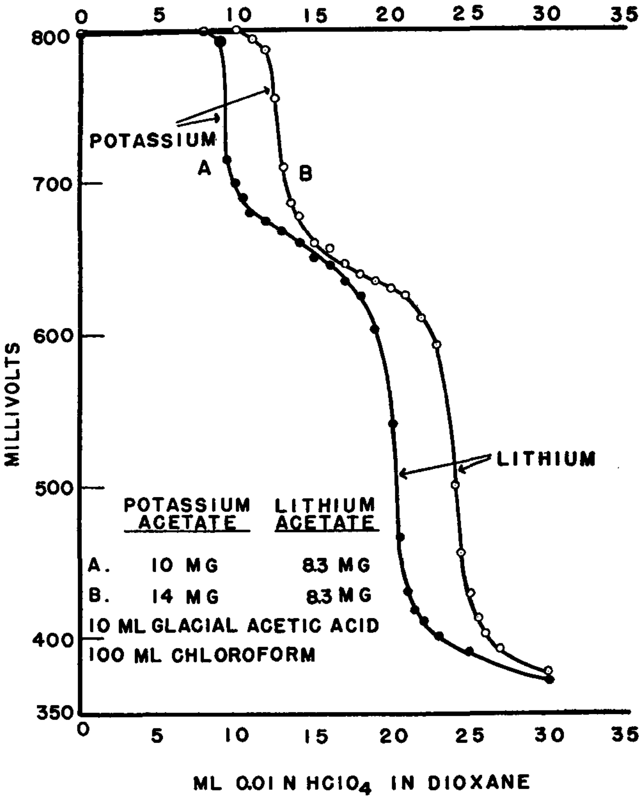

Figure 2. Titration of Lithium and Potassium Acetates

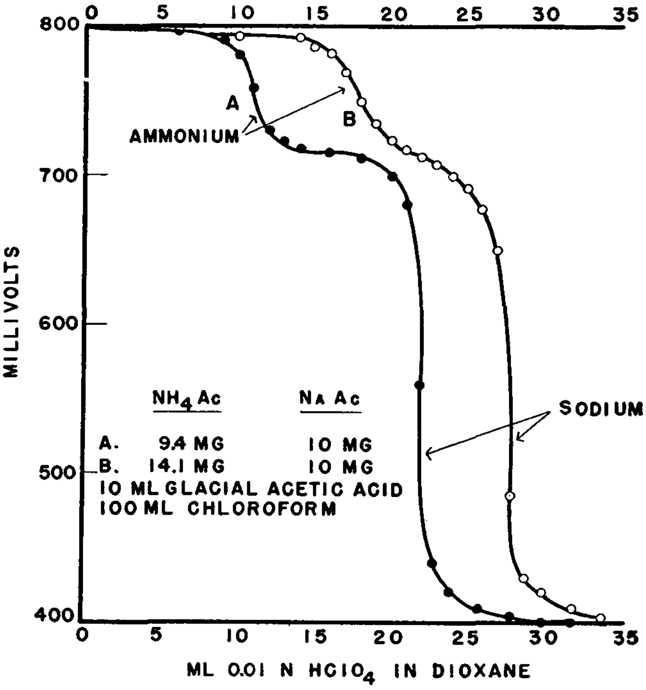

Figure 3. Titration of Ammonium and Sodium Acetates

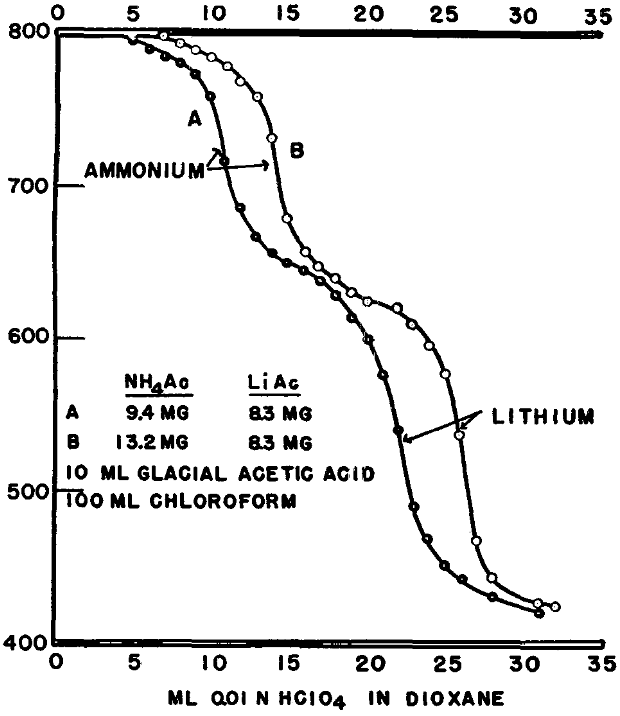

Figure 4. Titration of Lithium and Ammonium Acetates

certain inorganic cations by differential potentiometric titration when dissolved in an acetic acid–chloroform solvent. The titrant used was $0.01N$ perchloric acid in *p*-dioxane.

EXPERIMENTAL

The first system studied concerned the differentiation between sodium and potassium as their acetate salts.

Solutions of 750 mg. of potassium acetate and 600 mg. of sodium acetate in 100 ml. of glacial acetic acid were prepared. Two milliliters of each solution were pipetted into a 150-ml. beaker and 100 ml. of chloroform was added. The solution was titrated potentiometrically with $0.01N$ perchloric acid in *p*-dioxane using a glass–calomel (sleeve-type) electrode system.

Two distinct inflections were obtained, as shown in curve *A*, Figure 1. The first potentiometric break was due to the potassium acetate and the second to the sodium salt. These breaks were identified by keeping the quantity of the sodium salt constant while increasing the amount of the potassium salt and repeating the titration (curve *B*). The end points observed corresponded to the calculated quantities of titrant.

When a solution of potassium and lithium acetates in a similar solvent mixture was titrated, curves similar to those for sodium and potassium salts were obtained (Figure 2). The potentiometric titration of a solution containing 8 mg. of ammonium acetate and 12 mg. of sodium acetate in a mixture of 4 ml. of glacial acetic acid and 100 ml. of chloroform showed two distinct breaks (Figure 3). Titration curves of ammonium and lithium acetates are presented in Figure 4.

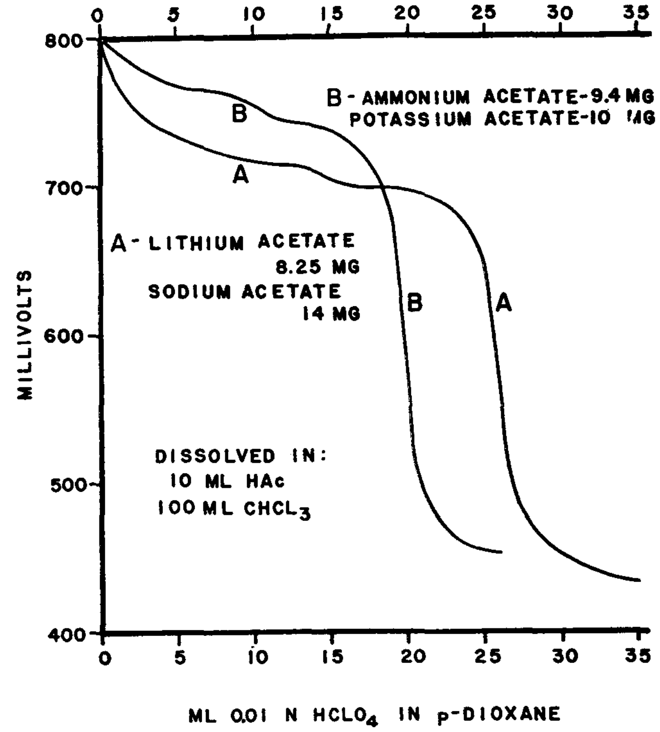

Figure 5. Titration of Ammonium-Potassium and Lithium-Sodium Acetates

The results of these experiments (Figures 1 to 4) show that both potassium and ammonium acetates have greater basic strength than either sodium or lithium acetate, when titrated in an acetic acid–chloroform medium. When attempts were made to differentiate between ammonium and potassium acetates, only one potentiometric inflection was obtained indicating that these salts are of nearly the same basic strength in this solvent system (Figure 5).

Cations of inorganic acetates, which were studied, are listed below in groups I and II. It was possible to differentiate the cations of group I, from any of those in group II. However, the cations listed in group II could not be differentially determined in the presence of each other.

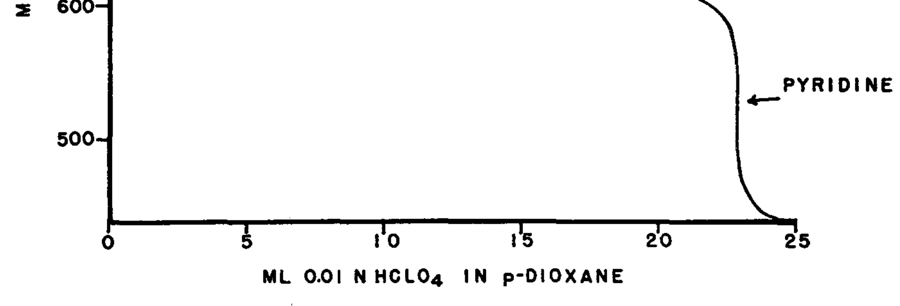

Figure 6. Titration of Organic and Inorganic Bases

Group I	Group II	
Ammonium	Barium	Nickel
Potassium	Cadmium	Silver
	Calcium	Sodium
	Lead	Strontium
	Lithium	Zinc
	Magnesium	

An interesting aspect of these experiments is the fact that ammonium acetate behaves as a base of strength comparable to potassium acetate in acetic acid–chloroform solution, while in water ammonium hydroxide is a much weaker base than potassium, sodium, or lithium hydroxide.

In another series of experiments, alkali metal salts were differentially titrated in the presence of organic bases. In one example, a solution containing 15 mg. of potassium acetate, 15 mg. of pyridine, and 4 mg. of *n*-butylamine was prepared in 10 ml. of glacial acetic acid and 100 ml. of chloroform. This mixture was titrated potentiometrically with 0.01*N* perchloric acid in *p*-dioxane (Figure 6).

It is evident from this graph that potassium acetate is a stronger base than either *n*-butylamine or pyridine. When ammonium acetate was substituted for potassium acetate, a similar curve was obtained. However, when cations of group II were used instead of those of group I, the basicity of their acetate salts was found equal to that of *n*-butylamine but stronger than pyridine (Figure 6).

CONCLUSIONS

The experiments described have shown that ammonium and potassium acetates behave as stronger bases than other inorganic acetates studied in the nonaqueous solvent system of acetic acid–chloroform. Thus, a differential titration of sodium acetates and potassium acetates was accomplished.

ACKNOWLEDGMENT

The authors are indebted to E. G. E. Shafer for his valuable suggestions, and to Esther Critelli for preparing the graphs.

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Analytical Aspects of Reactions of 2-(2-Pyridyl)-benzimidazole And 2-(2-Pyridyl)-imidazoline with Iron(II)

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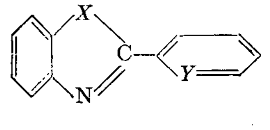
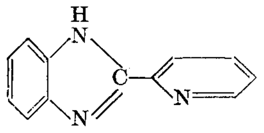
The compounds, 2(2-pyridyl)-benzimidazole and 2(2-pyridyl)-imidazoline, of interest because of their structural similarity to 2,2′-bipyridine and *o*-phenanthroline, were prepared and their reactions with metal cations tested. Both were found to give color reactions with copper(I), copper(II), cobalt(II), iron(II), and iron(III). Most notable were those with iron(II), with which deep red-purple colored complexes were formed. These complexes were studied spectrophotometrically and found to have maximum absorbances at 490 mμ for 2-(2-pyridyl)-benzimidazole at pH 5.7 and 560 mμ for 2-(2-pyridyl)-imidazoline at pH 9.0. The molar extinction coefficients for the 2-(2-pyridyl)-benzimidazole and 2-(2-pyridyl)-imidazoline are 3800, and 7800, respectively. The iron complexes could also be extracted with isoamyl alcohol, thus increasing the sensitivity of the color reaction.

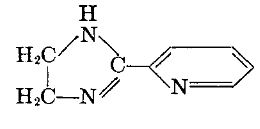
IN THE course of a study of analytical reagents of the type



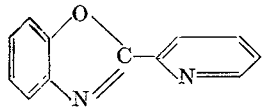
where X = O, S, NH and Y = C—OH, C—SH, and N (*7–9*), 2-(2-pyridyl)-benzimidazole(I) and 2-(2-pyridyl)-imidazoline(II) were prepared and tested. These compounds were of interest because of their structural similarity to bipyridine and *o*-phenanthroline, reagents for iron. Also, because certain substituted phenanthrolines and diquinolyl did not exhibit reaction with iron, ostensibly because of steric hindrance of the groups adjacent to the nitrogens, the question arose whether the benz- portion of the benzimidazole would exert sufficient hindrance to prevent complex formation. In this, comparison with the imidazoline with no steric hindrance should be revealing.



I



II



III

2-(2-Pyridyl)-benzoxazole(III) was also prepared for purposes of comparison because it was felt that the benz- portion of the benzoxazole would offer less hindrance to coordination reactions of the nitrogen than would occur in the corresponding benzimidazole nitrogen (*2*).

The reactions of 2-(2-pyridyl)-benzimidazole and 2-(2-pyridyl)-imidazoline with metal ions were found to be quite similar to those of bipyridine and *o*-phenanthroline in that a red complex with iron(II) was formed readily. The colored complex was readily extractable with isoamyl alcohol. That the analogous benzoxazole(III) did not give any reaction with iron(II) was attributed to the lower basicity of the oxazole nitrogen as compared to the imidazole nitrogen.

REAGENTS AND APPARATUS

Preparation of 2-(2-Pyridyl)-benzimidazole. The procedure outlined here is essentially that of Leko and Vlajinats (*3*).

One mole (123 grams) of α-picolinic acid and 1 mole (108 grams) of o-phenylenediamine were allowed to react in a distilling flask immersed in an oil bath kept at a temperature of 175° to 185° C. for 3 hours. The flask was then stoppered and the product distilled under atmospheric pressure at a temperature of about 310° C. Direct heat rather than immersion in an oil bath was used for heating the flask for distillation. The resultant product, recrystallized twice from an alcohol-water mixture, gave a melting point of 216° to 219° C. (literature melting point, 216° to 218° C.). The compound was slightly soluble in water and very soluble in ethyl alcohol, isoamyl alcohol, chloroform, carbon tetrachloride, benzene, and ether.

Preparation of 2-(2-Pyridyl)-imidazoline. The procedure outlined here is essentially the same as that for 2-(2-pyridyl)-benzimidazole with few exceptions.

One mole (123 grams) of α-picolinic acid and 1 mole (60 grams) of ethylenediamine were allowed to react in a distilling flask immersed in an oil bath kept at a temperature of 150° to 160° C. for 4 hours. The flask was then stoppered and the product distilled under atmospheric pressure using direct heat. The resultant product was a thick, green, oil which was induced, by scratching the side of its container, to crystallize as white crystals. The compound was recrystallized twice from petroleum ether (boiling point 90° to 100° C.), giving a melting point of 96° to 98° C. Oxley and Short give 97° to 98° C. (*6*).

The compound is soluble in water and virtually all organic solvents.

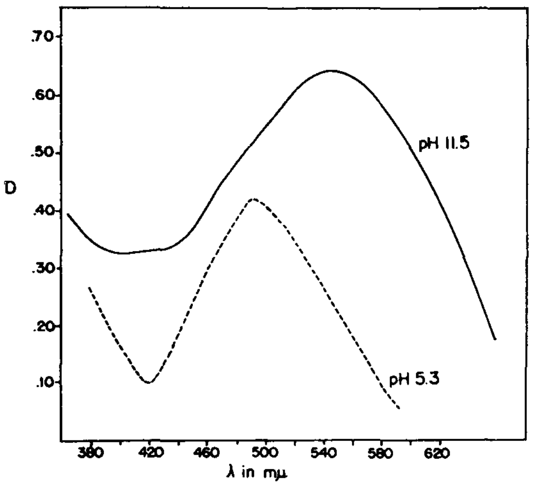


Figure 1. S-T Curves for Iron Complex of 2-(2-Pyridyl)-benzimidazole in Aqueous Solution at Different pH Values

10γ of iron per ml.

Reagent Solutions. Reagent solutions of 2-(2-pyridyl)-benzimidazole and 2-(2-pyridyl)-imidazoline having the concentration of 20 mg. per ml. were prepared in 95% ethyl alcohol and used in aliquots as needed. An alcoholic solution of either reagent is stable for an indefinite period.

Metal Ion Solutions. Reagent grade nitrates of aluminum, barium, bismuth, cadmium, calcium, cobalt, copper, indium, lead, magnesium, manganese, mercury, nickel, potassium, silver, sodium, strontium, and zinc, the chloride of tin, and the sulfate of niobium were used to make solutions which contained 50 mg. of metal per ml. for use in testing for the specificity of the reagents as well as for interferences to the reactions with iron.

Standard Iron Solution. Exactly 3.500 grams of Thorn Smith standard ferrous iron(II) ammonium sulfate (99.9%) pure was dissolved in 500 ml. of iron-free distilled water. A few drops of concentrated sulfuric acid were also added to prevent hydrolysis. The resulting solution had an iron concentration of 1.00 mg. per ml.

Buffer Solution. A sodium acetate–acetic acid buffer solution was prepared by dissolving 225 grams of sodium acetate and 250 ml. of acetic acid in distilled water and diluting up to 1 liter (*1*). This buffer solution was used to maintain the pH between 5.0 and 5.8 in the solutions to be analyzed spectrophotometrically.

Hydroxylamine Reducing Solution. A 10% aqueous solution of C.P. hydroxylamine hydrochloride was used as the reducing agent in all of the runs. One milliliter of this solution was added in each determination to keep the iron in a reduced state.

Isoamyl Alcohol. The isoamyl alcohol used as the extracting solvent was dried over calcium chloride and fractionated through a 3-foot helices-packed distilling column.

Apparatus. All pH measurements were carried out using a Model G Beckman pH meter.

All colorimetric measurements were made with the Beckman DU quartz spectrophotometer equipped with 1.000-cm. cells.

REACTIONS WITH METALS

Qualitative tests of 2-(2-pyridyl)-benzimidazole with several metals were carried out in both acidic and basic media. Results show that only mercury(II), copper(I), iron(II), and cobalt(II) give any perceptible reaction in either acid or basic regions. Mercuric ion gives a white precipitate, copper and cobalt give light brown to orange colors, the iron(II) gives an intense red color. No noticeable reaction in either acidic or basic media was observed with any of the other metals tested. The qualitative procedures used for the above tests are those outlined by Irving, Butler, and Ring (*1*).

Qualitative tests were performed in both acidic and basic media with 2-(2-pyridyl)-imidazoline. Results show that only mercury(II), copper(I), cobalt(II), iron(III), and iron(II) give any perceptible reaction in either acid or basic media. Mercury(II) ion gives a white precipitate, cobalt, iron(III), and copper(I) ions give a deep yellow color, copper(II) gives a deep bluish color, and iron(II) gives a red-purple color. No noticeable reaction in either acidic or basic media was observed with any of the other metals tested.

STRUCTURE OF THE METAL COMPLEXES

Leko and Vlajinats (*4, 5*) have prepared and analyzed the silver, copper(II), and mercury(II) salts of the 2-(2-pyridyl)-benzimidazole and give the following formulas based upon the analysis: $(C_{12}H_9N_3).CuCl_2$, $(C_{12}H_9N_3).HgCl_2$, and $(C_{12}H_8N_3).Ag$.

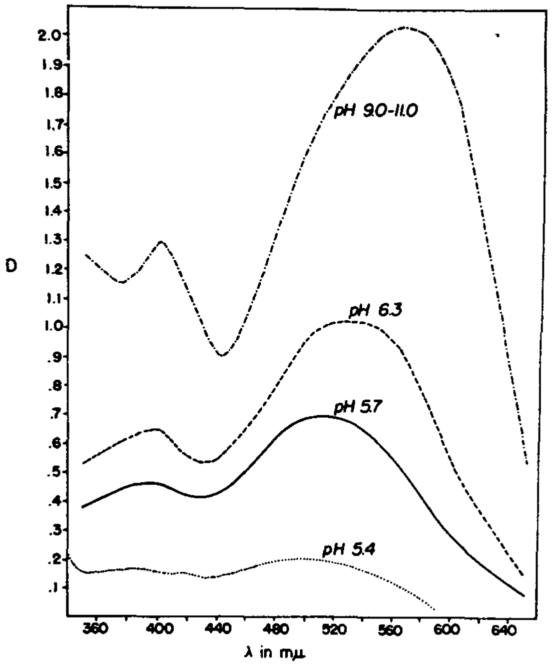


Figure 2. S-T Curves for Iron Complexes of 2-(2-Pyridyl)-imidazoline at Different pH Values

20γ of iron per ml.

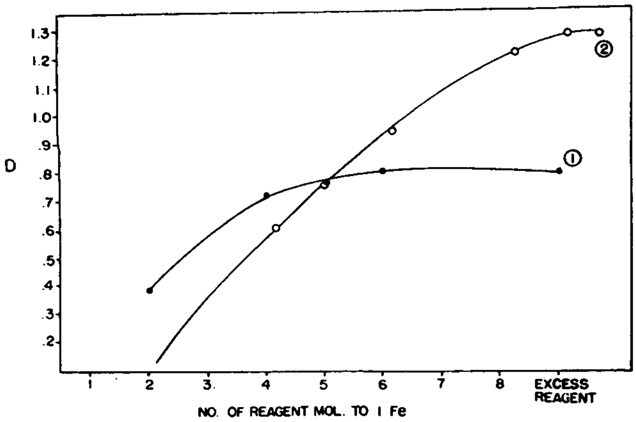
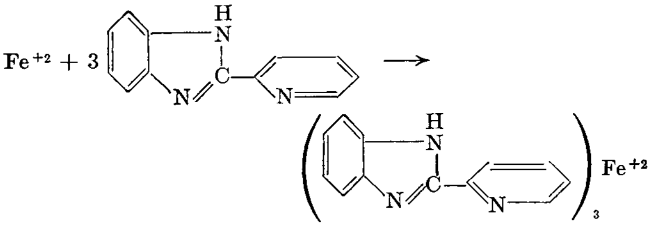


Figure 3. Iron-Reagent Ratio Curves

1. Iron with 2-(2-pyridyl)-benzimidazole
2. Iron with 2-(2-pyridyl)-imidazoline

Some of the commonly used anions were tried to precipitate the iron complex. Only the perchlorate of the ferrous salt of 2(2-pyridyl)-benzimidazole gave a precipitate in neutral solution. The resultant brick-red salt gave the following analysis: reported, C = 51.0%, H = 3.31%, and N = 15.2%; calculated, C = 51.3%, H = 3.2%, and N = 15.1%. This corresponds to the formula $Fe(C_{12}H_9N_3)_3(ClO_4)_2$, indicating that three reagent molecules react with each iron molecule, much as does 2-(2-bipyridine) and *o*-phenanthroline.



Several anions were added to solutions containing the iron complex of 2-(2-pyridyl)-imidazoline, but no precipitate was obtained in either acidic or basic solution. However, since the reagent has the same general structure as the 2-(2-pyridyl)-benzimidazole as well as the same general reactive properties, it can be assumed that the iron complex has the same structure.

COLOR REACTION

When an alcoholic solution of the reagents 2-(2-pyridyl)-benzimidazole or 2-(2-pyridyl)-imidazoline is added to an aqueous solution containing iron(II) ions, an intense red color is formed. The alcoholic solution of the reagent has no color itself. However, the intensity of the color produced depends upon several varying factors. The effect and nature of these factors are listed below.

Wave Length of Maximum Absorption. Spectral transmittance curves were run on aqueous solutions of the iron complexes of 2-(2-pyridyl)-benzimidazole and 2-(2-pyridyl)-imidazoline from 350 to 700 mμ at several pH values. From the curves represented in Figures 1 and 2 it can be seen that the wave length of maximum absorption varies with the pH. For the 2-(2-pyridyl)-benzimidazole iron complex, 490 mμ was found to be the wave length of maximum absorption in the pH region from 4.0 to 6.0 and 545 mμ as the wave length of maximum absorption in the pH range above pH 10.

For 2-(2-pyridyl)-imidazoline-iron complex, 560 mμ was chosen as the wave length of maximum absorption for the pH range 9.0 to 11. The wave length of maximum absorption as well as the color sensitivity increases with the pH.

Effect of pH. Several measurements were taken on the colored 2-(2-pyridyl)-benzimidazole complex at various pH values 2.0 to 10. The absorbance increased with pH to a maximum at pH 5.0. The density reading remained constant in the pH range 5.0 to 6.0. Above this pH value a turbidity was noted which persisted until a pH of 11 was reached, where a deep purple color was obtained and could be maintained above this pH. It was found that the pH could be maintained between 5.0 and 6.0 by the use of a sodium acetate–acetic acid buffer solution. The higher pH's were obtained by using sodium acetate and sodium hydroxide solution.

The color intensity of the red-purple complex of iron and 2-(2-pyridyl)-imidazoline increased with the pH until a pH of 9 was reached. Above pH 9 the sensitivity of the color reaction did not increase but was maintained at a constant value.

Reducing Agents. Sodium sulfite and hydroxylamine hydrochloride were tried as reductants for the iron. It was found that the hydroxylamine hydrochloride was most satisfactory for the reduction of iron or for the prevention of any oxidation of the reduced iron. The relatively small amounts used and the speed of reduction warrant the use of this reductant.

Color Stability. A solution of the iron complex of 2(-2-pyridyl)-benzimidazole, containing hydroxylamine as a reductant and kept at a pH of about 5.5 with the buffer solution, was found to give the same extinction reading after standing in a stoppered flask for a period of weeks. This same solution at pH 11 to 12 could be preserved only for about 24 hours.

A solution of the iron complex of 2-(2-pyridyl)-imidazoline containing hydroxylamine as a reductant and maintained at a pH of 9.0 with sodium acetate and sodium hydroxide would give a reproducible extinction reading after standing in a stoppered flask for not longer than a week.

Effect of Reagent Concentration. In Figure 3, it has been attempted to show the effect on the color development of the variation of the reagent 2-(2-pyridyl)-benzimidazole–iron ratio from 2 to 1 up to 8 to 1 and also the effect of a great excess. As can be seen from the plot, it is necessary to have a reagent-iron ratio of 6 to 1 for maximum color development rather than the stoichiometric ratios of 3 to 1. A greater excess of reagent over the 6 to 1 ratio has no effect upon the absorbance readings. The gradual slope of the curve also points out that a relatively weak complex is being formed.

The relative stability of the 2-(2-pyridyl)-imidazoline appears to be even less than that of the 2-(2-pyridyl)-benzimidazole since, in order to obtain maximum color development at any pH, there must be a great excess of reagent present. The relative position of this curve also appears in Figure 3. Both of these curves were run at pH values giving maximum color development.

Table I. Study of Bleaching Effect

Metal Ion Tested	Concn. of Fe, γ/Ml.	Concn. of Metal Ion, γ/Ml.	D_A[a]	D_B[b]
Blank	500	0	0.343	0.150
Copper	500	500	0.050	0.130
Nickel	500	500	0.005	0.080
Cobalt	500	500	0.030	0.115
Zinc	500	500	0.300	0.150
Manganese	500	500	0.345	0.150
Copper	0	500	0.004	0.005
Nickel	0	500	0.001	0.001
Cobalt	0	500	0.001	0.002
Zinc	0	500	0.000	0.000
Manganese	0	500	0.000	0.000

[a] *A* = 2-(2-pyridyl)-benzimidazole.
[b] *B* = 2-(2-pyridyl)-imidazoline.

The preliminary study of interferences revealed that a number of metal ions, such as copper, cobalt, and nickel, seemed to consume reagent. Although these ions did not themselves exhibit any characteristic color when mixed with the reagents, their presence resulted in more or less bleaching the iron-reagent color. When a great excess of reagent was used, no bleaching effect was noted. A study was made of this reaction.

Equimolar concentrations of the ferrous ion and of the metal to be studied in relation to iron were added to a volumetric flask.

Sufficient reagent solution was added so that there was a ratio of 3 moles of reagent to 1 of iron. One milliliter of hydroxylamine solution was also added, the pH was adjusted to 5.2 in the case of the 2-(2-pyridyl)-benzimidazole and to pH 9.0 in case of the 2-(2-pyridyl)-imidazoline, and the solution was diluted to volume. This serves as a sort of competition reaction. A blank was run on the iron, and separately upon each tested metal as well to ensure that no erroneous reading would be obtained from a color produced by that metal. The absorbance readings were recorded for each experiment and the results can be seen in Table I.

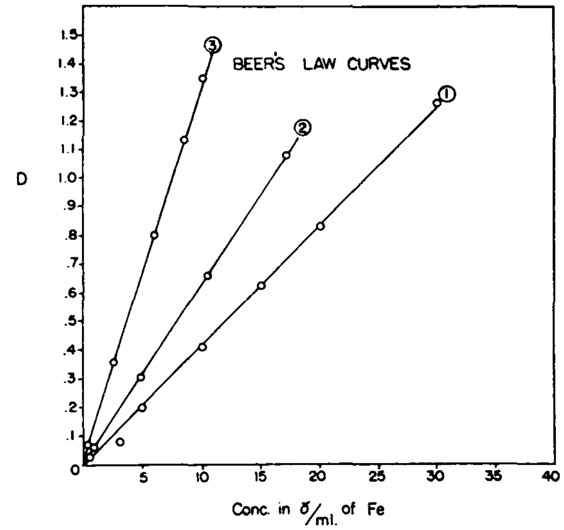


Figure 4. Beer's Law Curves

1. 2-(2-Pyridyl)-benzimidazole, 490 mμ, pH 5.2
2. 2-(2-Pyridyl)-benzimidazole, 545 mμ, pH 11.0
3. 2-(2-Pyridyl)-imidazoline, 560 mμ, pH 9.0

Sensitivity. The conformity of the colored solution of 2-(2-pyridyl)-benzimidazole to Beer's law was studied over a concentration range from a lower limit of about 0.5γ of iron per ml. to a maximum concentration of about 40γ per ml. Beer's law was followed very closely as can be seen from Figure 4. From this, then, a molecular extinction coefficient was calculated to be about 2600 at 490 mμ (pH 5.5) and 3800 at 545 mμ (pH 11).

The 2-(2-pyridyl)-imidazoline iron complex also conformed to Beer's law in a concentration range from 0.05 to about 15γ of iron per ml. as shown in Figure 4. The molecular extinction coefficient calculated at 560 mμ (pH 9) was 7800. This compares favorably with 2-2'-bipyridine and *o*-phenanthroline (*10*).

Effect of Diverse Ions. The 2-(2-pyridyl)-benzimidazole and 2-(2-pyridyl)-imidazoline method for the colorimetric determination of iron is comparatively free from interference by most of the anions and cations. Only a few cause any appreciable interference as can be seen from Table II.

2-(2-PYRIDYL)-BENZIMIDAZOLE. The method used for the study of the effect of diverse ions on the color development was as follows:

In each case, exactly 2 ml. of the standard iron solution containing 200γ of iron are added to a 100-ml. volumetric flask (this is 20γ of iron per ml.). Then 6 ml. of the sodium acetate–acetic acid buffer solution were added. Varying amounts of the metal ion solution to be studied were then added. An alcoholic solution of the reagent was added until the deep red color of the iron complex appeared to remain constant, and then a slight excess was added. The absorbance of the resultant solution was then read at 490 mμ after about 15 minutes. All readings were compared with the Beer's law curve to determine the extent of interference. The results can be observed in Table II.

For the determination of iron in solution, the following ions may be present in concentrations of at least 600γ without causing an error greater than 2%: aluminum, acetate, bismuth, barium, cadmium, calcium, chloride, cobalt, copper, indium, fluoride, iodide, lanthanum, lead, magnesium, manganese, nickel, niobium, phosphate, potassium, sodium, strontium, sulfate, tin, and zinc.

The ions which give serious interference are silver, mercury(II), and tartrate, when present in any concentration.

2-(2-PYRIDYL)-IMIDAZOLINE. Essentially the same procedure was followed in the study of the effect of diverse ions with 2-(2-pyridyl)-imidazoline as was followed with the 2-(2-pyridyl)-benzimidazole. The only exceptions were that only half the concentration of iron was used (10γ of iron per ml.) and that the study was made at pH 9.0 and 560 mμ. The results observed can be seen in Table II.

The ions which give serious interference are mercury(II), silver, and the metals which give hydroxides at this pH. These latter interferences may be eliminated by the use of some complexing agent as tartrate or citrate.

Effect of Extraction. The extraction of the ferrous complex of 2-(2-pyridyl)-benzimidazole was tried with several of the common organic extractants. The only satisfactory extractant found was isoamyl alcohol. Isoamyl alcohol will extract the colored complex completely at any pH. It was found that when the color from 100 ml. of solution was extracted into 10 ml. of the isoamyl alcohol, the sensitivity was increased threefold. This increase in the sensitivity allowed, by extraction, the extension of the lower limit of the concentration range in aqueous solution to about 0.05γ per ml.

The ferrous complex of 2-(2-pyridyl)-imidazoline was not extracted by any of the organic extractants tried, at any pH. However, the colored complex would extract into isoamyl alcohol if perchlorate ion were present. This probably means that the perchlorate of the complex is more soluble in isoamyl alcohol than it is in water. The following equations best describe the reaction [R = 2-(2-Pyridyl)-imidazoline]:

$$Fe^{+2} + SO_4^{--} + 3R \xrightarrow{OH^-}$$

$$FeR_3SO_4 \text{ (not soluble in isoamyl alcohol, but soluble in water)}$$

$$FeR_3SO_4 + 2ClO_4^- \xrightarrow{OH^-} FeR_3(ClO_4)_2 +$$

$$SO_4^{--} \text{ (soluble in water but more soluble in isoamyl alcohol)}$$

The extraction with isoamyl alcohol also increases the sensitivity of the color reaction with this reagent.

RECOMMENDED PROCEDURES

For the determination of iron with 2-(2-pyridyl)-benzimidazole, transfer to a 50-ml. volumetric flask an aliquot of the unknown solution containing a quantity of iron which is within the concentration range illustrated by the Beer's law curve (Figure 4). Then add 1 ml. of the 10% solution of hydroxylamine hydrochlo-

Table II. Effect of Ions

Ion plus Fe	Concn. of Ion, γ/Ml.	Max. Interference[a], % Fe A	B
Aluminum	600	None	None
Acetate	600	None	None
Barium	600	None	None
Cadmium	600	2	None
Calcium	600	1	None
Chloride	600	2	2
Cobalt	300	1	1
Copper	600	1	5
Fluoride	600	None	None
Indium	600	None	None
Iodide	600	None	None
Lead	600	1	5
Magnesium	600	None	None
Manganese	600	None	None
Mercury	70	Interferes	Interferes
Nickel	600	1	None
Niobium	600	None	None
Nitrate	600	1	None
Perchlorate	600	Interferes	None
Potassium	600	None	None
Silver	70	Interferes	Interferes
Sodium	600	None	None
Strontium	600	1	None
Sulfate	600	None	None
Tartrate	100	Interferes	None
Tin	300	3	2
Zinc	600	None	None

[a] A = 2-(2-pyridyl)-benzimidazole, B = 2-(2-pyridyl)-imidazoline.

ride to reduce the iron. Add approximately 3 to 5 ml. of the sodium acetate–acetic acid buffer solution, or until the pH is between 5.0 and 6.0. Add an alcoholic solution of the reagent until the red color of the complex appears to be constant and then add a slight excess (2 ml.). Bring the volume up to 50 ml. with distilled water, and read the extinction values on the spectrophotometer.

When the concentration of iron is below about 2γ per ml., the sensitivty can be increased by extracting the color from the prepared aqueous solution into isoamyl alcohol. Depending on the concentration of iron as well as the volume of aqueous solution the volume of extractant can be varied.

Essentially the same procedure is used for the determination of iron with 2-(2-pyridyl)-imidazoline, except that the determination is made at about pH 9 rather than at pH 5; pH 9 is obtained by the use of about 2 grams of sodium acetate and a few drops of 3*N* sodium hydroxide. Also, when extracting with isoamyl alcohol, an excess of perchlorate (as sodium perchlorate) should be used to the amount of iron present, so that the colored complex will extract.

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Use of Molybdates for Estimating Amount of Olefinic-Type Hydrocarbons in Air

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The estimation of micro quantities of olefinic hydrocarbons is important in studies of atmospheric pollution, as these hydrocarbons oxidize under proper conditions in the air, giving compounds that can cause crop damage, eye irritation, and reduced visibility. The gradual color change from yellow to green accompanying reduction of complex and simple molybdates in acid media has been used by others for measuring the amount of carbon monoxide in air. The same color change can be produced in molybdates by olefins and forms the basis for a method of measuring the approximate amount of C_3 and heavier olefinic hydrocarbons in the air. The method employs inexpensive equipment and should find useful application in air-pollution work.

THE determination of olefinic-type unsaturation in petroleum products by bromine number has long been a routine test. However, the method was developed for relatively large quantities of sample and large proportions of olefins in the sample. The determination of micro quantities of olefinic hydrocarbons is important in studies of atmospheric pollution, since these hydrocarbons can oxidize under proper conditions in the air and cause crop damage, eye irritation, and reduced visibility (*2, 5–7, 10, 12*). Large tonnages of olefins are released daily into the air from petroleum production, refining, and marketing, as well as from automobiles. Hydrocarbons have been shown to be the largest source of organic material emitted to atmosphere in Los Angeles (*10*). There is at present no established method for determining the amount of olefinic-type hydrocarbons in the air.

Polis, Berger, and Schrenk (*15*) of the U. S. Bureau of Mines devised a colorimetric procedure for determining relatively large amounts of carbon monoxide in air using phosphomolybdic acid. It was shown that certain olefins were effective in causing color production in this test. An extremely sensitive test for carbon monoxide was described by Shepherd (*16*). This test was based on color production in silica gel impregnated with ammonium molybdate, sulfuric acid, and palladous sulfate. Although certain precautions are taken in practice to prevent olefin interference, the impregnated silica gel can be made to give an intense green color with olefins (*17*). A procedure was developed in this laboratory for estimating minute amounts of C_3 and heavier olefinic-type hydrocarbons in the air based on a similar color reaction. This involved development of a highly sensitive, yet stable, molybdate reagent.

PRINCIPLE OF METHOD

If an air sample is drawn through a finely divided caustic material as, for instance, Ascarite, various acidic substances such as carbon dioxide, nitrogen dioxide, aldehydes, organic acids, peroxides, sulfur dioxide, and hydrogen sulfide can be largely removed. Furthermore, if the air which has been drawn through Ascarite is sampled in a freeze-out trap such as that proposed by Shepherd (*18*) which uses liquid oxygen refrigerant, carbon monoxide and hydrogen will not be collected because of their extremely low boiling points. All olefins, however, except ethylene and propylene, exist as solids at this low temperature. Ethylene cannot be collected in substantial quantity because of its appreciable vapor pressure, although some may be retained in the freeze-out trap under proper conditions. A certain amount of acetylene also may be collected in the trap (*18*). Since the largest general source of acetylene to atmosphere is the automobile exhaust, in which acetylene constitutes about 5% of the hydrocarbons (*13*), neglecting acetylene can introduce only a small error. Olefins in automobile exhaust gases comprise approximately half of the hydrocarbons from this source.

A colorimetric reagent was devised with a view to maximum sensitivity and as uniform a color intensity for various types of

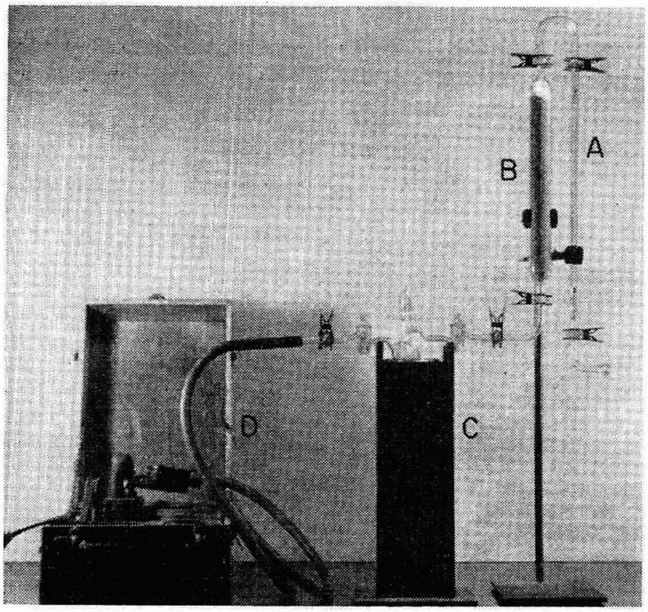

Figure 1. Air Sample Collection Apparatus

A. **Rotameter**
B. **Ascarite tube**
C. **Shepherd trap**
D. **Wilson pump**

olefins as possible. The reagent contained sodium molybdate, palladous sulfate, acetic acid, and sulfuric acid. It can be rapidly and simply prepared. The golden color gradually turns blue-green in the presence of reducing agents, the color becoming more intense with time. Palladium salts catalyze the reduction of molybdates (*16*, *22*). Palladous chloride could not be used because of the desensitizing effect of chloride ions (*17*). Work by Shepherd (*16*) indicated that palladous sulfate and a low pH are essential to high reagent sensitivity. Acetic acid has been shown previously to facilitate color development in heteropoly acids (*4*, *9*) and was found necessary in this preparation. Sodium molybdate was used instead of ammonium molybdate because the reagent slowly darkens in the presence of a large amount of ammonium ions. As described later, phosphomolybdic acid can be substituted for sodium molybdate, based on molybdenum content, with approximately the same sensitivity toward olefins and same wave length of maximum light absorption. Reduction of hetěropoly acids at low pH has previously been shown to result in absorption peaks characteristic of simple molybdates (*3*, *20*).

Several excellent reviews of the subject of simple and complex blues have been written by Wright with Mellon (*21*), Mellon (*14*), and Woods with Mellon (*20*).

REAGENTS AND APPARATUS

The best grades of chemicals available were used in this work. Of the several brands of reagent-grade glacial acetic acid tested, Mallinckrodt was found to be of the requisite purity for preparation of a stable colorimetric reagent. Acetylene (welding grade, 99.5% + purity, negative silver nitrate test) was further purified by passage through three bubblers containing 20% sodium bisulfite, two bubblers containing concentrated sulfuric acid, and dried through Ascarite.

The Beckman DU quartz spectrophotometer with cells of 1-cm. path length was used for all absorbance readings. The slit width at 685 mμ was 0.08 mm. All spectrophotometer readings were taken at approximately 25° C. (room temperature).

The apparatus used to collect the air samples is shown in Figure 1. $ 18/7 glass joints were used throughout the construction. The Ascarite tube was 1.5 inches in diameter by 12 inches long. The experimental setup used in transferring the air sample from the Shepherd trap to the 2-liter flask is shown in Figure 2.

CALIBRATION OF THE SODIUM MOLYBDATE REAGENT

It was found that the colorimetric reagent used by Polis *et al.* was not sufficiently sensitive for the desired purposes and responded too selectively to some unsaturates. Furthermore, peak absorptions varied within the range of 675 to 800 mμ for the different unsaturates and for different concentrations of the same unsaturate.

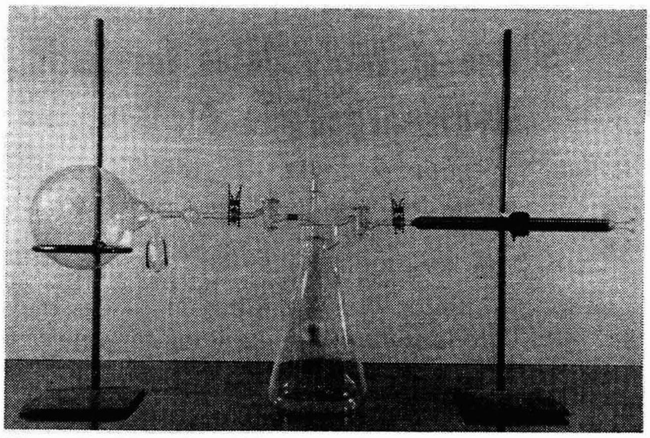

Figure 2. Transfer of Air Sample from Shepherd Trap to 2-Liter Flask

Table I. Various Compounds Tested

Expt. No.	Compound	Amt. of Reagent Placed in Flask, Ml.	Amt. of Compound/Liter of Reagent, Mg.	Absorbance, 685 Mμ	Extinction Coeffic., $E^{g./l.}_{1\,cm.}$
166c	Ethylene	20	11.4	1.30	113
171a	Ethylene	20	5.7	0.800	140
176c	Propylene	15	11.4	1.02	89
176d	Propylene	15	5.7	0.490	85
166a	1-Butene	15	10.6	0.810	76
172d	1-Butene	15	7.6	0.720	95
172e	1-Butene	15	15.2	1.20	79
172f	1-Butene	20	17.1	1.30	76
172g	1-Butene	42	5.4	0.450	83
172h	1-Butene	22	5.0	0.448	89
175a	1-Butene	20	7.9	0.645	81
179a	1-Butene	15	11.4	0.910	80
172a	*cis*- and *trans*-2-butene	15	10.6	1.45	136
172b	*cis*- and *trans*-2-butene	15	7.6	1.10	145
172c	*cis*-2-Butene	15	10.6	1.45	136
166d	Isobutylene	15	10.6	0.480	46
167d	Isobutylene	15	10.6	0.345	33
171b	Butadiene	15	10.6	0.465	44
174a	Butadiene	15	10.6	0.525	49
165a	1-Hexene	20	16.8	1.52	90
165b	1-Hexene	25	13.5	1.27	94
171c	1-Hexene	20	8.4	0.715	85
165c	2-Methyl-1-pentene	30	11.3	1.45	128
171d	2-Methyl-1-pentene	30	9.0	0.930	103
173h	4-Methyl-1-pentene	25	13.4	1.00	75
173g	2-Ethyl-1-butene	25	13.8	1.14	83

[a] Based on olefin content by bromine number of 31.5% weight.

A new molybdate reagent was developed in order to overcome these difficulties. This reagent was prepared as follows:

Composition of Molybdate Reagent. 6.1 grams of c.p. sodium molybdate; 25 ml. of distilled water; 0.35 ml. of c.p. palladous sulfate solution, aqueous 10%, (purchased from Fairmount Chemical Co., Inc., Newark, N. J.); 40 ml. of reagent-grade glacial acetic acid (Mallinckrodt); and 40 ml. of c.p. concentrated sulfuric acid were mixed. To facilitate solution of the ingredients, they should be added in the order given. Water at room temperature may be used for cooling, but ice water causes crystallization to occur. The reagent can be stored for several weeks in a glass-stoppered bottle in the laboratory but turns green if exposed to sunlight.

Gaseous olefins were tested with this new reagent in a 2-liter round-bottomed flask having a 1-cm. diameter neck which could be closed by a small piece of rubber tubing and a screw clamp. Introduction of samples was accomplished by evacuating the flask and inserting the gas by means of a greased 0.25-ml. calibrated glass syringe (B-D Yale No. 1/4 YT) and needle, through the wall of the rubber tubing. An ungreased syringe was used for introducing liquid substances to be tested, the vacuum in the flask allowing rapid dispersion of the small quantities as vapors. In most cases it was necessary to dilute the liquid substances to be tested with an acid-treated paraffin (*n*-heptane and 2,2,4-trimethylpentane were used) because of the extreme sensitivity of the reagent.

Following introduction of the sample, the flask was brought to atmospheric pressure slowly by admitting laboratory air through a tube containing Ascarite and Hopcalite (approximately 20-mesh Hopcalite, Mine Safety Appliances Co., Pittsburgh, Pa.). This was to remove any carbon monoxide, ozone, olefin, and nitrogen dioxide contaminants from the air. A measured amount of reagent was added and the contents of the flask were swirled up around the walls. The flask was immersed to a depth of 1 inch in a water bath at 60° ± 2° C. for 1.5 hours. At the end of 0.75 hour in the bath the contents were swirled. After the 1.5-hour heating period, the flask was again swirled and allowed to cool for 15 minutes. The occasional mixing was necessary in maintaining a homogeneous color and creating a certain amount of new surfaces. Blanks on similarly filtered laboratory air in a 2-liter flask were run in conjunction with all of the tests. No color change was ever observed in any of the blanks. Results of calibrating tests on olefins and other substances are shown in Table I.

Experience indicated that reproducibility of results was better when the test was carried out at 60° C. rather than merely allowing the reaction to proceed at room temperature. It is presumed that a more uniform contact of reagent and gas occurs at the elevated temperature because of thermal currents within the flask and because of the scrubbing action of condensing vapors from the reagent. The 1.5-hour heating period was selected in order to give an optimum color commensurate with a minimum time and the amount of olefins collectable in a practical air sample. The increase in color intensity of the reagent gradually becomes less and less with length of heating, but was not observed to become completely asymptotic with time even after several hours at 60° C.

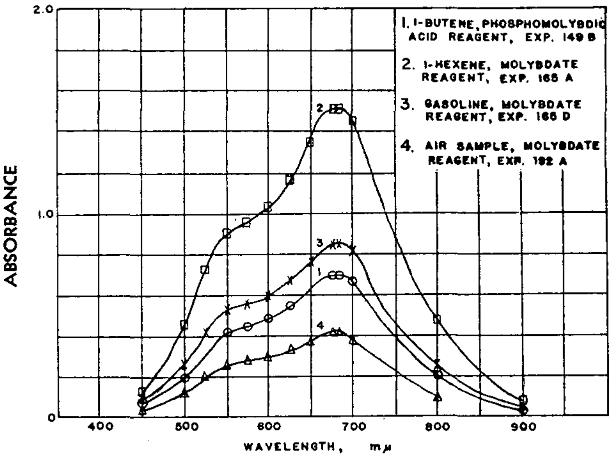

Figure 3. Absorption Spectra, Reactions at 60° C.

The data for 1-butene and for 1-hexene in Table I showed that the color intensity for the olefins conformed to Beer's law. Several representative spectrograms for this work are presented in Figure 3. Included in Figure 3 is a curve for one of several tests in which phosphomolybdic acid was substituted for sodium molybdate based on molybdenum concentration. A peak absorption at 685 mμ was exhibited regardless of whether phosphomolybdic acid or sodium molybdate was used. The peak wave length was not influenced by the type of olefin tested or its concentration. However, varying the palladous sulfate or molybdenum concentrations from the optimum specified was found to produce radical changes in relative color intensities for straight chain with respect to branched-chain and cyclic olefins.

It will be observed from Table I that with the exception of isobutylene, the various olefins tested were found to have extinction coefficients between 59 and 145. Isobutylene was slightly lower than the other unsaturates. The collective olefins in an ethyl gasoline were found to fall within the range of extinction coefficients for the various individual olefins tested. The average $E^{g./l.}_{1\,cm.}$ for the eight tests with 1-butene was 82. The standard deviation of a single measurement was ±7. The average $E^{g./l.}_{1\,cm.}$ for all tests with unsaturates in Table I including iso-

with Sodium Molybdate Reagent

Expt. No.	Compound	Amt. of Reagent Placed in Flask, Ml.	Amt. of Compound/Liter of Reagent, Mg.	Absorbance, 685 Mμ	Extinction Coeffic., $E^{g./l.}_{1\,cm.}$
173e	Cyclohexene	25	16.0	1.15	72
173a	1-Heptene	25	14	1.10	79
173b	2-Heptene	25	14	1.12	80
173c	3-Heptene	25	14	0.820	59
173d	1-Octene	25	14.4	1.10	76
173f	1-Decene	25	15.2	1.45	95
175c	Acetylene	15	5.3	1.08	203
175d	Acetylene	15	7.1	1.45	204
165d	Ethyl gasoline	15	8.0[a]	0.850	106[a]
166b	Ethyl gasoline	15	12.0[a]	0.900	75[a]
179c	Hydrogen	15	165	0.735	4
176a	Carbon monoxide	40	19.9	1.50	75
176b	Sulfur dioxide	20	91	0.215	2
175b	Formic acid	15	2040	0.990	0.5
174d	Benzene	15	5850	0.063	0.01
174c	Methanol	11	7260	0.043	0.006
174b	Formalin (37%)	15	7200	0.382	0.05
206a	Acrolein	70	6	1.01	169
206b	Ammonia	50	500	0.000	. . .

butylene but excluding butadiene, ethylene, and acetylene, was 87 with a standard deviation of ±27.

The following substances may be found in polluted air:

Constituent	P.P.M. by Volume in Air	Reference
Carbon dioxide	300	(*8*)
Hydrogen	100	(*8*)
Carbon monoxide	3.5–23	(*10*)
Methane	2	(*1*)
Nitrous oxide	0.5	(*19*)
Hydrocarbons	0.2–1.1	(*10*)
Organic acids	0.70 (max.)	(*11*)
Oxides of nitrogen	0.08–0.4	(*10*)
Aldehydes	0.07–0.4	(*10*)
Ozone	0.06–0.3	(*10*)
Sulfur dioxide	0.05–0.3	(*10*)
Formaldehyde	0.04–0.9	(*10*)
Ammonia	0.007 (max.)	(*10*)
Acetylene	Present	(*10, 18*)

Hydrogen sulfide cannot normally be detected in Los Angeles air.

The extinction coefficients for hydrogen, sulfur dioxide, formic acid, benzene, methanol, formaldehyde, and ammonia were extremely low and, therefore, these compounds should not provide interference in routine air analyses for olefins. Similar data for a variety of substances tested with the Bureau of Mines phosphomolybdic acid reagent has been published (*15*). Nitrous oxide was mixed with ethylene in a volume ratio as high as 360 to 1 and found not to influence noticeably the normal color intensity reaction of the ethylene alone. Nitrogen dioxide if not carefully removed during air sampling will give low analyses for olefins. Tests with mixtures of nitrogen dioxide and 1-butene showed that 1 volume of nitrogen dioxide reduced the color intensity equivalent to 5.3 volumes of 1-butene.

ESTIMATING OLEFINIC-TYPE HYDROCARBONS IN AIR SAMPLES

Procedure. Atmospheric samples were drawn through a rotameter and 20- to 30-mesh Ascarite and were collected in a Shepherd trap immersed in liquid oxygen (Figure 1). It is advisable to test the trap for leaks prior to sampling by using a manometer and observing whether the trap will maintain a vacuum. The amount of sample collected depends on the quantity of olefin contained in the air. Three liters per minute for 1 hour provided the usual sample. The Dewar must be maintained full of liquid oxygen during sampling for maximum freeze-out efficiency.

The freeze-out trap containing the air sample was immersed in liquid nitrogen and allowed at least 20 minutes to come to temperature. The pressure in the trap was then rapidly reduced to about 5 mm. of mercury to remove ozone (vapor pressure at −196° C. between 0.01 and 0.1 mm.) and carbon monoxide (vapor pressure at −196° C. = 400 mm.) which might be in the residual gas within the trap. Olefins were found by actual test not to be perceptibly removed in this treatment.

The Shepherd trap under 5-mm. of mercury pressure was next connected to an evacuated 2-liter round-bottomed flask. A tube, 1.5 inches diameter by 12 inches long, containing Hopcalite protected from moisture by Ascarite on both ends, was connected to the other arm of the Shepherd trap. The trap was then warmed to 60° C. by insertion into a 2-liter wide-mouthed Erlenmeyer flask containing warm water (Figure 2). After temperature equilibrium was reached (about 20 minutes in the water), the valves to the flask were opened, equalizing the pressure between trap and flask. Laboratory air was slowly allowed to enter the evacuated 2-liter flask through the Hopcalite and freeze-out trap. This transferred the olefins from the trap into the flask and simultaneously brought the flask to atmospheric pressure. A measured amount of the molybdate reagent, usually about 20 ml., was added to the olefins in the 2-liter flask through a ground-glass side stopper. Directions for preparing the reagent were given previously.

The contents of the flasks were swirled up around the walls and the flask was placed in a water bath at 60° ± 2° C for 1.5 hours. The flask was removed from the bath after 0.75 hour and the contents were swirled up around the walls, after which the flask was replaced in the bath. After the 1.5-hour heating period, the contents of the flask were again swirled up around the walls and the flask was allowed to cool for 15 minutes. The color intensity was then determined at 685 mμ using a Beckman DU spectrophotometer. This measurement was made against a blank on the original reagent run simultaneously in the same manner as the sample, using a 2-liter flask of air filtered through Hopcalite. A number of samples can be analyzed simultaneously by one chemist, since the equipment needed is inexpensive.

In calculating the olefin content of the air sample, $E_{1\,\text{cm.}}^{\text{g./l.}}$ was taken as 87 ± 27. An average extinction coefficient for *all of the* olefins tested was used because a prorated extinction coefficient based on the amounts of individual olefins encountered in the air was not available. Calculations indicated that at air concentrations the limits of accuracy of the method were within a factor of two of the values given by the following equation:

$$\text{P.p.m. by weight } C_3 \text{ and heavier olefins} = \frac{\text{absorbance at 685 m}\mu \times \text{ml. reagent} \times 9.7}{\text{liters of air sampled}}$$

The air sampled was assumed to be at 25° C. The estimated accuracy for the method included the error in $E_{1\,\text{cm.}}^{\text{g./l.}}$ of ±27 as well as the error derived from collection efficiency tests on prepared blends of 1-butene in air to be described later. No attempt was made to evaluate the error in analysis due to collection of small amounts of ethylene and acetylene.

Synthetic Blends of Olefins in Air. Tests were conducted on synthetic blends of 1-butene in air, in order to obtain an idea of the efficiency of the freeze-out technique. These blends were made in a small Plexiglas house which had previously been constructed for other experiments (*10*). Air from a blower was metered through an orifice at 500 cubic feet per minute, the flow rate being accurately checked with an anemometer. 1-Butene from a cylinder was metered through a glass constriction meter and blended with the air prior to the orifice in order to obtain mixing. The mixture was then distributed into the house through a ductwork around the floor. The blends were prepared in the evening when local air pollution was shown by test to be at a minimum. Sampling of the contents of the house was accomplished through glass tubing extending into the house. Blank samples were simultaneously taken of the air used in the blends. Results are shown in Table II.

Table II. Synthetic Blends of 1-Butene in Air

Expt. No.	1-Butene in Air, P.P.M. Vol.	Butene Recovered[a], %
186a	0.9	79
186b	0.9	80
187a	0.4	65
187b	0.4	103
188	0.8	99
	Av.	85

[a] 180-liter air samples were analyzed.

Under conditions normally used for air sampling, the average recovery of 1-butene was 85%. The two results for blends containing 0.4 p.p.m. of 1-butene were more erratic than the others. This was due to the extreme difficulty in preparing accurate blends of such small quantities of hydrocarbon in air. Since the accuracy in preparing the blends was not known, the collection efficiency could not be evaluated as precisely as desired. The tests showed that a reasonable recovery can be obtained and the olefin is not destroyed or appreciably reacted with the Ascarite used to filter the air.

The question as to which of the lighter olefins might escape complete capture in the Shepherd trap at air concentrations because of appreciable vapor pressures was determined experimentally, since no satisfactory conclusion could be arrived at by calculation. A blend containing 0.4 p.p.m. of mixed olefin gases in air was prepared in the Plexiglas house. The olefin mixture was composed of equal volumes of ethylene, propylene, 1-butene, and isobutylene. Sampling of the contents of the house was carried out as described for 1-butene. Mass spectrometer analysis showed the following amounts of olefins to be present in the gas within the trap: ethylene, $\lesssim$ 0.001% volume; propylene, 0.013% volume; and butylenes, 0.023% volume. All experimental evidence indicated that as an approximation for air sampling, the C_3

Table III. C_3 and Heavier Olefinic-Type Hydrocarbons in Air in Los Angeles County

Expt. No.	Date	Hour	Location	Olefins, P.P.M. Wt.
121a	6-18-52	8:00 A.M.-10:00 A.M.	Dominguez	0.12
121b	6-18-52	8:00 A.M.-10:00 A.M.	Downtown L.A.	0.47
121c	6-18-52	11:00 A.M.-12 Noon	Downtown L.A.	0.01
122	6-20-52	10:30 A.M.-12:30 P.M.	Downtown L.A.	0.21
129	7-1-52	11:00 A.M.- 1:00 P.M.	Downtown L.A.	0.12
131	7-3-52	10:00 A.M.-12 Noon	Downtown L.A.	0.33
132a	7-9-52	10:30 A.M.-12:30 P.M.	Downtown L.A.	0.16[a]
132b	7-9-52	10:30 A.M.-12:30 P.M.	Downtown L.A.	0.18[a]
134a	7-11-52	8:30 A.M.- 9:30 A.M.	Downtown L.A.	0.30
134b	7-11-52	11:00 A.M.-12 Noon	Downtown L.A.	0.15
191	10-27-52	7:30 A.M.-8:30 A.M.	Downtown L.A.	0.60
192a	1-1-53	7:00 A.M.- 9:00 A.M.	Vernon	0.11
192b	1-1-53	9:00 A.M.-11:00 A.M.	Vernon	0.03
192c	1-1-53	11:00 A.M.- 1:00 A.M.	Vernon	0.04
192d	1-1-53	7:00 A.M.- 8:00 A.M.	Pasadena	0.70
192e	1-1-53	8:00 A.M.- 9:00 A.M.	Pasadena	0.56
192f	1-1-53	9:00 A.M.-10:00 A.M.	Pasadena	0.14
192g	1-1-53	10:00 A.M.-11:00 A.M.	Pasadena	0.09
207a	7-23-53	9:30 A.M.-10:30 A.M.	Downtown L.A.	0.34[a]
207b	7-23-53	9:30 A.M.-10:30 A.M.	Downtown L.A.	0.32[a]

[a] Analyses run in duplicate.

and heavier olefins are collectable, although this may be somewhat variable depending on concentrations present in the air.

Use of the Plexiglas house was also made in evaluating the efficiency for removal of nitrogen dioxide by the 20- to 30-mesh Ascarite. Tests showed that when air contained 0.7 p.p.m. of nitrogen dioxide, less than 1% of it was collected in the Shepherd trap under regular sampling conditions.

Results of Air Analyses. Analyses were made for C_3 and heavier olefinic-type hydrocarbons in the air in Los Angeles. Results are shown in Table III.

The olefin content of the air was greater as a rule in the early morning than in the late morning and afternoon. This may have been due to a gradually increasing oxidation in the presence of sunlight and probably, in larger part, to meteorological factors.

A weight ratio of olefins to carbon monoxide of 0.075 was obtained from analyses of automobile exhaust gases under average driving conditions in Los Angles (*13*). Carbon monoxide was measured in the air at Pasadena on New Year's Day and at Los Angeles on July 23, 1953, using the method of Shepherd (*16*). Based on carbon monoxide analyses and the 0.075 ratio, the olefin content of the air was calculated to be:

Pasadena, January 1, 1953	
7:00- 8:00 A.M.	0.53 p.p.m. by wt.
8:00- 9:00 A.M.	0.50 p.p.m. by wt.
9:00-10:00 A.M.	0.13 p.p.m. by wt.
10:00-11:00 A.M.	0.10 p.p.m. by wt.
Los Angeles, July 23, 1953	
9:30-10:30 A.M.	0.32 p.p.m. by wt.

These calculated values and the amounts of C_3 and heavier olefins found by analyses in Table III agreed well with a factor of 2. The general agreement between calculated and analyzed values, in conjunction with meteorological data, indicated that the C_3 and heavier olefins in these cases originated primarily from automobile exhausts.

SUMMARY AND CONCLUSIONS

A molybdate reagent in strongly acid medium was developed to give a maximum sensitivity toward olefins. The newly developed reagent was nearly equally sensitive, on a weight basis, to all olefins and was not influenced by aromatics or saturates. Gasoline produced color commensurate with its bromine number. Varying the palladous sulfate or sodium molybdate contents of the reagent from the specified proportions varied the sensitivity for straight-chain olefins with respect to cyclic and branched-chain olefins.

The molybdate reagent was adapted for use in air sampling. Air samples were drawn through 20- to 30-mesh Ascarite and collected in freeze-out traps using liquid oxygen refrigerant. Relatively inexpensive laboratory equipment is involved. Disregarding trace amounts of ethylene and acetylene which may be collected, estimates can be made of the C_3 and heavier olefin content of the air within a factor of about two. Typical results on air in Los Angles County showed that C_3 and heavier olefinic-type hydrocarbons occasionally exceed 0.5 p.p.m. by weight.

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Micromethod for Measuring Reaction Rates in Solution Under Moderate Pressures

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Rapid heat transfer and easy temperature control are achieved by the use of glass melting point capillaries as reaction vessels for measuring rates of reaction in solution. The sealed capillaries will hold pressures up to 71 atmospheres or more. Details are given for the reaction of acetic acid with aniline to form acetanilide. The rate constants, expressed in mole fractions and reciprocal minutes, are 0.0767 ± 0.0050 at 150°, 0.193 ± 0.013 at 175°, and 0.392 ± 0.028 at 200° C. The activation energy is roughly 13,000 calories per mole.

GOLDSCHMIDT and Wachs (2) have measured the rate of formation of acetanilide from acetic acid and aniline in the presence of a large excess of aniline and have found that the reaction was second order with respect to acetic acid. Their rate expression, recalculated for minutes, is $v = 6.5 \times 10^{-4}\,(\mathrm{HOAc})^2$ at 100° C., in which the concentration of acetic acid is expressed in moles per liter. The rate of the reaction in the presence of an excess of acetic acid has not been reported, although acetanilide is usually prepared in this manner. In the present investigation the rate was determined at 150°, 175°, and 200° C. These temperatures are above the boiling point of the mixture at atmospheric pressure. The reaction was first order with respect to acetic acid and first order with respect to aniline. Sufficient experimental data are not yet available to discuss the difference between the apparent reaction order of the acetylation in an excess of aniline and in an excess of acetic acid.

Table I. Analysis of Glacial Acetic Acid

Weight of Sample, Mg.	0.1*N* NaOH, Ml.	Acetic Acid, %
7.93	1.314	99.5
7.36	1.218	99.4
7.23	1.191	98.9
10.08	1.665	99.2
6.38	1.059	99.7
9.63	1.598	99.7
9.08	1.496	98.9
		Average, 99.33 ± 0.31

When the rate of a reaction in solution under pressure is investigated, the use of macro quantities of the reagents imposes several problems. The reagents must be preheated before mixing, and the temperature after mixing must be adjusted quickly. Samples must be removed in such a way that flash evaporation of the sample is avoided, and the samples must be chilled quickly in order to arrest the reaction. The portion of the sampling line which protrudes from the reaction vessel must be cleaned before the next sample is taken. If there is a mistake or an accident in the sampling or in the analysis, the entire reaction must be repeated. If several reaction vessels are used, each containing a single macro sample for analysis, the rate of heat transfer is still too slow, and temperature regulation is difficult. Micromethods have the advantages of accurate sampling, rapid heat transfer, comparatively good temperature control, and ease of operation.

For the microdetermination, macro quantities of the reagents were weighed accurately and mixed, in a ratio of very nearly 2 moles of acetic acid to 1 mole of aniline. Samples were charged to the tared melting point capillaries, which were sealed and reweighed. The capillaries were placed in a thermostatically controlled oil bath for the desired lengths of time and then chilled in an ice bath. The contents of the capillary were dissolved in acetone, and the acetic acid was titrated to the phenolphthalein end point with 0.1*N* sodium hydroxide.

This micromethod can be used for reactions which take place in a single liquid phase and are negligibly slow at room temperature. No change could be detected in the composition of a mixture of acetic acid and aniline in 6 hours at room temperature. Nevertheless, as a further precaution, the mixture and the filled capillaries were kept in a refrigerator except for the time when the materials were being manipulated. No test was made on the bursting strength of the capillaries. However, a sample of liquid carbon dioxide was contained by a capillary at 30° C., corresponding to a pressure of 71.1 atmospheres, absolute.

EXPERIMENTAL

Ordinary melting point capillaries, approximately 15 cm. long and 1 mm. in diameter, were modified in the following way: The mid-point of the capillary was sealed so that one half of the capillary could act as the handle and the other half as the reaction chamber. The open tip of the reaction chamber was heated and drawn out to a diameter of about 0.1 mm. The resulting reaction chamber was approximately 4 cm. long, exclusive of the narrowed tip. The tube was weighed to the nearest 0.01 mg. with the usual precautions of a weighing of this accuracy. The upper end of the reaction chamber was warmed above a microburner, and the tip was dipped into the solution. As the chamber cooled, 6 to 12 mm. of liquid was drawn up into the tube. Care was taken not to warm the portion of the reaction chamber which would later be in contact with the reaction mixture.

A more elegant filling technique would be to evacuate all of the capillaries at the same time and force the solution into them at slightly less than atmospheric pressure. Void space in the capillaries should not be excessive, but should allow for expansion of the liquid.

The fine tip of the capillary was sealed, and the capillary was reweighed to the nearest 0.01 mg. The capillary was immersed in the thermostatically controlled bath for the desired length of time, to the nearest 0.2 second. The capillary was then chilled in a bath of ice and water. For analysis, the capillary was wiped off, cleaned with acetone, and rewiped. The reaction chamber was scratched in several places with a piece of Carborundum, rewashed, and crushed with a stirring rod under 3 ml. of acetone in a thick-walled test tube of approximately 10-ml. capacity. Acetone was used in order to prevent any possible inclusion of acetic acid in the acetanilide. The acetic acid was titrated to the phenolphthalein end point with 0.1*N* sodium hydroxide, using a calibrated 5-ml. buret graduated in 0.01-ml. divisions. A blank determination on a crushed capillary showed no detectable alkali in the glass.

As a check on this technique, the glacial acetic acid was analyzed from samples which were weighed and sealed in this manner. The results are shown in Table I. The mean of these analyses is 99.33%, and within 95% confidence limits calculated statistically by Student's distribution (4) the mean is 99.33 ± 0.31%. The mean of two macrodeterminations was 99.4%.

The remaining starting materials were analyzed according to more conventional procedures. Water in the acetic acid was determined by titration with Karl Fischer reagent and found to be 0.27, 0.357, and 0.356%. This left some unaccounted material in the acetic acid. Therefore, water was assumed to be in the range of 0.27 to 0.67%. This assumption affected the determination of the rate constants by adding only 0.03% to the relative error. The aniline was water white and remained so for several weeks. The initial boiling point was 179.5°, and 95% of the aniline distilled within a 0.5° range. Therefore, the aniline was

Table II. Data for Reaction at 150° C.

Time, Minutes	HOAc, %	$\log_{10}\frac{(HOAc)}{(PhNH_2)}$	Completed, %
0	...	0.30103	0
0	...	0.30103	0
5	49.63	0.36215	24.2
5	49.71	0.36129	23.0
10	45.51	0.41657	39.3
10	46.11	0.40763	35.8
15	42.57	0.46795	48.4
15	42.40	0.46947	49.8
20	40.34	0.51718	56.3
20	40.43	0.51488	56.0
30	37.43	0.60215	66.7
39.92	35.37	0.68568	75.0
55	33.53	0.78815	80.5
55	33.40	0.79745	81.0
78	31.72	0.93949	87.0
78	31.77	0.93504	86.9
90	31.00	1.02437	89.6
120	30.27	1.13896	92.2
120	30.27	1.13897	92.2
180	29.70	1.26126	94.2
300	29.46	1.32921	95.1
1115	29.71	1.25909	94.2
1115	30.31	1.13281	92.0
2695	29.09	1.45417	96.4
2695	29.09	1.45777	96.4

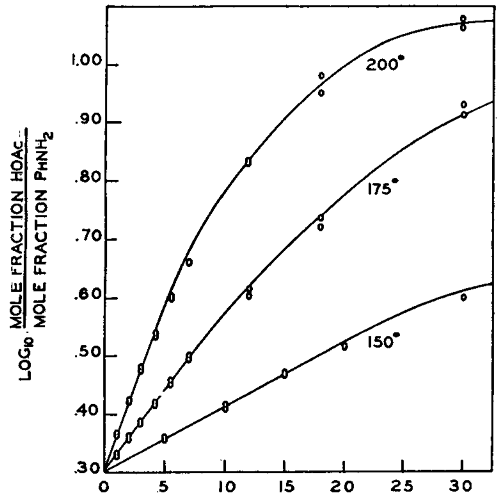

Figure 1. Plot of $\log_{10}\frac{\text{Mole Fraction HOAc}}{\text{Mole Fraction } PhNH_2}$ vs. Time

assumed to be pure, with an error equal to the error in the acetic acid assay.

CALCULATION

$$HOAc + PhNH_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2O + PhNHAc$$

$$\frac{-d(HOAc)}{dt} = \frac{-d(PhNH_2)}{dt} = k_1\,(HOAc)\,(PhNH_2) - k_{-1}\,(H_2O)(PhNHAc)$$

By the method of analysis which was used, the relative error in the equilibrium constant was far greater than the relative errors in the initial values of $\log_{10}\frac{HOAc}{PhNH_2}$. For this reason, the approximate method of initial slopes was used to obtain the rate constants. If the rate of the reverse reaction is negligible in the early stages of the reaction, the rate expression becomes:

$$\frac{-d(HOAc)}{dt} = \frac{-d(PhNH_2)}{dt} = k_1\,(PhNH_2)\,(HOAc)$$

Table III. Data for Reaction at 175° C.

Time, Minutes	HOAc, %	$\log_{10}\frac{(HOAc)}{(PhNH_2)}$	Completed, %
0	...	0.30103	...
0	...	0.30103	...
1	52.33	0.33385	13.6
1	52.51	0.33219	12.9
2	49.73	0.36092	22.8
2	49.46	0.36417	23.8
3	47.73	0.38508	30.0
3	47.30	0.39096	31.5
4.25	45.31	0.41966	38.6
4.25	45.15	0.42218	39.2
5.5	43.41	0.45181	45.4
5.5	43.03	0.45893	46.7
7	41.19	0.49700	53.2
7	41.06	0.49989	53.7
12	37.05	0.61545	68.0
12	37.40	0.60304	66.8
18	34.39	0.73602	77.5
18	34.66	0.72112	76.5
30	31.98	0.91242	86.1
30	31.82	0.92939	86.7
90	29.71	1.25851	94.2
360	29.62	1.28033	94.5
360	29.82	1.23180	93.8
1085	29.31	1.37388	95.6
1085	29.83	1.22781	93.7

Table IV. Data for Reaction at 200° C.

Time, Minutes	HOAc, %	$\log_{10}\frac{(HOAc)}{(PhNH_2)}$	Completed, %
0	...	0.30103	...
0	...	0.30103	...
1	48.97	0.36981	25.5
1	49.60	0.36396	23.7
2	45.20	0.42123	39.0
2	44.96	0.42521	39.7
3	41.95	0.48035	50.6
3	42.31	0.47309	49.3
4.25	39.40	0.54121	59.7
4.25	39.59	0.53618	59.0
5.50	37.38	0.60360	66.8
5.50	37.45	0.60131	66.6
7	35.92	0.66082	72.1
7	35.89	0.66186	72.2
12	32.88	0.83454	82.8
12	32.94	0.82998	82.6
18	31.62	0.94998	87.4
18	31.34	0.98181	88.4
30	30.63	1.07733	90.8
30	30.72	1.06441	90.5
90	30.49	1.10045	91.4
90	30.34	1.12510	91.9
360	30.42	1.11190	91.6
360	30.46	1.10473	91.4
1159	30.12	1.16797	92.6
1159	30.44	1.10897	91.5

When concentrations are expressed as mole fractions, the equation can be rearranged to give:

$$d\log_{10}\frac{HOAc}{PhNH_2} = \frac{1}{2.303} \times \frac{a-1}{a+1+w} \times k_1\,dt$$

in which a is the ratio of the moles of acetic acid to moles of aniline in the original mixture, and w is the ratio of moles of water to moles of aniline in the original mixture. Thus a plot of $\log_{10}\frac{HOAc}{PhNH_2}$ against time will give a straight line, unless the reverse reaction becomes appreciable. The rate constant, k_1, equals $\frac{2.303 \times (a+1+w)}{(a-1)}$ times the slope of the straight line. The use of the mole fraction instead of moles per liter is unorthodox and not theoretically exact for the measurement of the rate constant in a liquid phase reaction. The slope of the lines in Figure 1 is not affected, but the slope should be multiplied by a term in inverse concentration units instead of the dimensionless expression $2.303 \times (a + 1 + w)/(a - 1)$. To express k_1 in liters per mole per minute instead of reciprocal minutes, it would be necessary to measure the density of the reaction mixture at 150°, 175°, and 200° C.

The original mixture was composed of 12.0837 grams of glacial acetic acid and 9.3126 grams of aniline, analyzed as shown above. The value of $2.303 \times \frac{(a+1+w)}{(a-1)}$ was $6.93 + 0.11$. From the known composition of the original mixture and the analyses of acetic acid in the reacted samples, $\log_{10} \frac{\text{HOAc}}{\text{PhNH}_2}$ was calculated for each sample. This quantity would have been more precise if the aniline were analyzed also. Toward the end of the reaction the determination of aniline by difference gives a quantity which is unduly affected by the experimental error in the analysis of acetic acid. The results of the analyses are shown in Tables II, III, and IV. The fourth column in each refers to the percentage of aniline which has been converted to acetanilide.

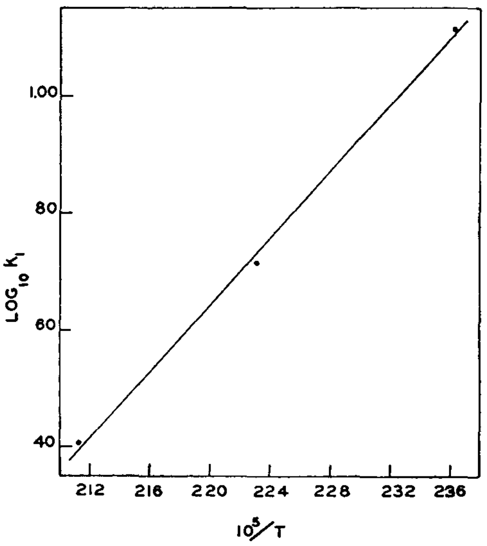

Figure 2. Plot of $\log_{10} K_1$ *vs.* $\frac{10^5}{T}$

The plot of $\log_{10} \frac{(\text{HOAc})}{(\text{PhNH}_2)}$ against time (Figure 1) gives a straight line through 15 minutes at 150°, 7 minutes at 175°, and 4 minutes and 15 seconds at 200° C. The slopes of the straight portions of the lines were obtained by the method of least squares. The composition at zero time was given the weight of two analyses, because the original materials were weighed and mixed accurately. The 95% confidence limits of the slopes were calculated statistically by Student's distribution (*4*). Multiplication of the slopes by 6.93 ± 0.11 (adding the relative errors) gave the values for k_1, which are summarized in Table V.

The plot of $\log_{10} k_1$ against $1/T$ (Figure 2) has a correlation coefficient (*3*) of 0.999 as compared with 1.000 for a truly linear array of points. Theoretically, k_1 should be expressed in moles per liter per minute or similar units. The use of mole fractions affects only the intercept and not the slope of this straight line, provided that the density of the mixture is constant over the temperature range. Using Student's distribution (*4*) on the least squares line, the slope is $-2850 \pm 1370°$ K. $= -0.4343\,E/R$, from which $E = 13{,}000 \pm 6250$ cal. per mole. This variation in the value of E is statistical and caused by the facts that only three points are plotted and the numerical values of $1/T$ are very close. The unknown variation in density is not included.

DISCUSSION

The precision of the measurements can be increased by including the direct analysis of aniline instead of analysis by difference. The significance of the slope can be increased to some extent by taking more measurements during the time that the kinetic plot is a straight line. However, at 200° C., the straight-line portion of the curve is so short that the very shortness limits the significance of the slope.

In general, this microprocedure can be expected to yield as accurate results as the macroprocedure, and far more easily. The individual analyses are as precise as the customary analyses of larger samples. The sampling procedure, in kinetic investigation such as this, is far more accurate, because each sample is self-contained from the time it is weighed until it has reacted and is ready for analysis. Reactions can be easily run in duplicate or triplicate. A highly important fact for rapid reactions is that the reaction mixture apparently comes to the proper temperature in a matter of seconds.

However, the temperature of this type of reaction must be computed, because only the temperature of the oil bath is measured. The temperature of the reaction is lower than that of the bath during the initial heating period of the capillary. The reaction temperature can become higher than the bath temperature if the heat of reaction can not be dissipated with sufficient rapidity. These compensating effects can be estimated if the rate of heat transfer through the capillary is known. An approximate method of measuring the rate of heat transfer is described below.

Table V. Values for k_1

Temp., ° C.	Slope	k_1	Relative Error, % In slope	 In k_1
150	0.01107 ± 0.00055	0.0767 ± 0.0050	5.0	6.6
175	0.0278 ± 0.0014	0.193 ± 0.013	5.0	6.6
200	0.0565 ± 0.0031	0.392 ± 0.028	5.5	7.1

The initial boiling point of the original reaction mixture in an Emich tube was found to be 133.6° C. Two Emich tubes were plunged into the oil bath at 137.1° C., and the boiling point was reached in 10.6 and 11.6 seconds, or an average of 11.1 seconds. If the specific heat of the mixture is assumed to be constant over the temperature range (admittedly a loose assumption), then

$$dT/dt = K(T_B - T), \text{ or } d\log_{10}(T_B - T)/dt = -0.4343K$$

in which T is the temperature of the contents of the tube at any time, and T_B is the temperature of the bath. This equation can be integrated to give $\log_{10}(T_B - T) = -0.4343Kt + K'$. From the data measured at 137.1° C., $T_B = 137.1°$ C., $T = 24°$ C. (room temperature) when $t = 0$, and $T = 133.6$, when $t = 11.1$ seconds. From these data, $0.4343K = 0.136$. With the bath at 141.5° and again at 148.4° C., the value of $0.4343K$ was 0.140. The average value of $0.4343K$ is 0.139, and $K = 0.320$. From this, an estimate can be made of the time necessary for the contents of the sealed capillary to rise within 1°, 2°, 3°, 10°, or within any range of 200° when the oil bath is at 200° C. and the room temperature is at 30° C. (as it was during the kinetic measurements).

$$-0.139\,t = \int_{30}^{x} d\log_{10}(200 - T)$$

in which x equals the final temperature of the contents of the capillary. Approximately 16 seconds should be required for the contents to rise to 199°, 14 seconds for 198°, 12.6 seconds for 197°, 8.9 seconds for 190°, 6 seconds for 175°, and 3.8 seconds for 150° C. The reaction of course, proceeds rapidly at these lower temperatures. By the same methods of calculation it is found that a capillary at 200° C. plunged into an ice bath requires approximately 4 seconds to cool to 60° and only 6 seconds to cool to 30° C., at which temperature the reaction is effectively stopped.

If sufficient thermodynamic data were available, it would be possible to calculate the rate of dissipation of the heat of reaction and the temperature of the reaction mixture during the reaction. In the absence of such data, the specific heat of the mixture will be assumed to be 0.47 cal. per gram per degree C. throughout the entire temperature range. The heat of reaction, calculated from heats of combustion at 20° C., will be assumed to be constant at $\Delta H = -11{,}300$ cal. per mole throughout the temperatures and pressures involved. The rate of heat transfer in the above experiments in the Emich tubes was $0.47 \times dT/dt$ cal. per gram per second. Since $dT/dt = 0.320\,(T_B - T)$, the rate of heat transfer was $0.47 \times 0.320 \times (T_B - T)$ cal. per gram per second.

If 2 moles of acetic acid and 1 mole of aniline, totaling 213 grams, are placed in capillaries, the rate of heat transfer is $213 \times 60 \times 0.47 \times 0.320 \times (T_B - T)$ cal. per minute. Thus, for every degree of difference between the tube contents and the bath, this mixture of acetic acid and aniline can transfer 1920 cal. per minute. The reaction between acetic acid and aniline is most rapid at the very beginning, before the concentrations have diminished. With the reaction rate constant equal to 0.392 min.^{-1}, it was calculated that at the beginning of the reaction 0.26 mole of acetanilide was being formed per minute. The heat evolved was therefore 2900 cal. per minute. To transfer heat at this rate, the reaction mixture must be 1.5° hotter than the 200° C. bath. Since the reaction is slower at lower temperatures, the mixture would be 0.7° hotter than the 175° bath and 0.3° hotter than the 150° C. bath. As the reaction progresses and becomes slower, the temperature difference would become less. Also, the temperature effect due to the heat of reaction tends to counteract the temperature lag when the cold tube is inserted into the hot oil bath.

Examination of Figure 1 indicates that the temperature lags had no appreciable effect on the results of the present investigation. The straight portions of the curves, determined by the method of least squares, point quite directly toward the origin, at which the abscissa is zero time and the ordinate is 0.30103. A calculation of the 95% confidence limits (*1*) of the ordinates of the least squares lines at zero time gives 0.3029 ± 0.0052 at 150°, 0.3038 ± 0.0031 at 175°, and 0.304 ± 0.0355 at 200° C.

Thus, the temperature lags had too small an effect on the course of the reaction to be detected by the methods of analysis which were employed. If the effects had been large, they could have been overcome by the use of capillaries with a diameter of 0.5 or 0.1 mm. and by correspondingly more refined micromethods of analysis.

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Improved Micro-Dumas Method and Apparatus

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The micro-Dumas method for the determination of nitrogen has been studied for the purpose of developing a reliable method for routine use. A convenient, unitized apparatus has been designed, and a well-defined procedure established. The sample is vaporized in a stream of carbon dioxide and the gases are passed over nickel oxide and nickel at 1000° C. to oxidize organic gases, hopcalite at 110° C. to oxidize carbon monoxide, and highly active copper oxide at 700° C. to oxidize traces of methane. The carbonaceous residue formed by pyrolysis of the sample is completely oxidized with oxygen, thus releasing any nitrogen which may be held by the residue. Nitrogen is collected, as usual, in an azotometer over potassium hydroxide solution. The volume of the nitrogen gas is measured by displacing and weighing an equal volume of mercury. The method is widely applicable and avoids certain errors encountered in the commonly used micro-Dumas methods. Results are presented to illustrate the accuracy, precision, and scope of the method.

THE nitrogen content of organic materials is generally determined by applying either the Kjeldahl or the Dumas method. While the Kjeldahl method is applicable to many substances and is attractive because of its simplicity, it is unreliable for the determination of nitrogen in certain materials, notably highly nitrated compounds and compounds containing nitrogen-to-nitrogen single bonds. These limitations of the Kjeldahl method have made the Dumas method indispensable in many laboratories.

Since the initial development of the micro-Dumas method by Pregl, a number of improvements in the method and apparatus have been described in the literature. The authors have developed a method which embodies many of these improvements and overcomes the major weaknesses of the commonly used micro-Dumas methods (*9*, *12*)—namely, incomplete oxidation of the methane which forms during sample pyrolysis (*14*) and incomplete combustion of carbonaceous sample residues which may contain nitrogen (*2*). The apparatus is unitized to increase the convenience of the analysis and to make maintenance of the equipment easier. Use is made of the nickel–nickel oxide tube filling suggested by Kirsten (*4*) to replace the conventional copper–copper oxide filling. Combustion of methane is ensured by an auxiliary combustion tube filled with highly active copper oxide (*8*). Pyrolysis of the sample is carried out by a traveling electric furnace (*3*, *10*) in a stream of carbon dioxide, and any carbonaceous residue is then completely burned in a stream of oxygen as described by Gonick *et al.* (*2*). This technique eliminates the necessity for mixing the sample with copper oxide or other oxidation aids when testing refractory compounds (*11*). Errors inherent in the measurement of the nitrogen volume in an azotometer filled with strong potassium hydroxide solution (*13*) are eliminated by use of the mercury-filled weight azotometer described by Koch *et al.* (*7*).

APPARATUS

A photograph of the apparatus is shown in Figure 1 and the apparatus is described schematically in Figure 2.

In order to maintain a satisfactorily low blank value it is necessary that the carbon dioxide used as a sweep gas contain not more

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than 0.01 volume % of nitrogen or other inert gases. This requirement is satisfied when carbon dioxide is prepared from the solid, liquefied in a pressure vessel essentially as described by Gonick *et al.* (*2*). The vessel used for this purpose has a capacity of 150 pounds of solid carbon dioxide, which provides a sufficient supply of gas to operate the unit for several years. Oxygen, for the combustion of residues remaining after the pyrolysis of sample, is obtained by the electrolysis of 2.5% potassium hydroxide solution in the all-glass apparatus shown in Figure 3. The generator functions automatically; the direct current, supplied to the electrodes at 8.7 volts by a suitable rectifier, is turned off when the pressure of the oxygen drives the electrolyte level below the anode and is turned on when the electrolyte level rises as a result of oxygen withdrawal. Hydrogen, simultaneously evolved, increases the pressure in the system until the mercury level in the by-pass valve drops below the sintered disk. Hydrogen then escapes through this disk until the pressure drops sufficiently to allow the mercury level to rise and reseal the disk.

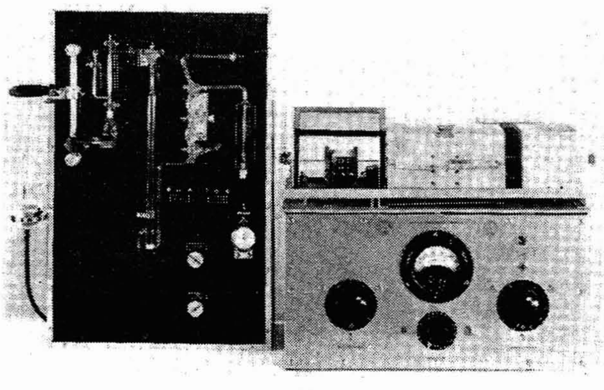

Figure 1. Unitized Micro-Dumas Apparatus

Oxygen Generator. The oxygen generator is prepared as follows: Place 1.7 liters of 2.5% potassium hydroxide solution in a 2-liter Erlenmeyer flask and boil for 5 minutes. Fit the flask with a 2-holed rubber stopper carrying two glass tubes, one of which extends to the bottom of the flask. Connect the glass tube which extends to the bottom of the flask to the exit line on the top of the 100-ml. oxygen bulb of the generator. Apply pressure to the solution in the flask through the other glass tube, support the generator in a horizontal position with the mercury bypass valve upward, and completely fill the generator with the caustic solution. Cap the open end and the sintered-glass plate of the mercury bypass line with rubber policemen, return the generator to an upright position, and release the pressure on the Erlenmeyer flask. Connect the electrodes to the rectifier and permit hydrogen to collect in the large bulb and to displace the liquid back into the Erlenmeyer flask until the liquid level in the large bulb drops to where it is even with the top of the small bulb. Cap the exit line of the oxygen bulb with a ball joint plug and remove the rubber policemen from the mercury bypass line. Add mercury to the mercury bypass line until the mercury level in the arm open to the atmosphere is approximately 5 cm. above the sintered disk. Connect the oxygen outlet to the apparatus and seal the spherical joint connection with sealing wax. Remove the liquid in the open arm of the bypass valve using an eyedropper.

Determine the purity of the generated oxygen by correcting the blank value (determination described subsequently) for the amount of nitrogen derived from the carbon dioxide. Less than 0.05 gram of mercury (0.01 volume % inert gases) should be obtained. If a higher value is obtained, draw oxygen from the generator by venting the gas to the atmosphere through stopcock *F* (Figure 2). To avoid any diffusion of air through *F*, close the stopcock when the pressure differential in the mercury bypass valve drops to 15 mm. above atmospheric. Permit oxygen to accumulate until the generator ceases to generate gas and redetermine the purity of the oxygen as before. Repeat until a satisfactory product is obtained.

Combustion Tube. The combustion tubes and fillings are described in Figure 4.

Pack the high temperature tube as shown, omitting the hopcalite. Hold the tube in a horizontal position and tap it to form a channel along the top of the nickel powder. Insert the tube into the furnaces as shown in Figure 2 and attach the inlet and tube closure fitting, which is made of stainless steel and is equipped with a screw cap to allow insertion of the sample. Adjust the temperature of the main furnace to 800° C. and that of the hopcalite furnace to 110° C. Pass carbon dioxide through stopcocks *G*, *F*, *E*, and *D* to remove air from the gas manifold, then turn stopcock *G* so that carbon dioxide flows through the tube. Attach stopcock *F* to a source of hydrogen, by means of rubber tubing, and pass a small amount of hydrogen through *F*, *E*, and *D* to flush the connecting tubing free of air. Turn off the carbon dioxide flow and pass hydrogen, at a rate of 10 to 20 ml. per minute, into the tube through stopcocks *F* and *G* until any nickel oxide is completely reduced. Sweep the hydrogen from the tube and manifold with carbon dioxide and, without removing the tube from the furnace, pack the exit end of the tube with hopcalite as shown in Figure 4. Insert the auxiliary tube, packed with precipitated copper oxide containing 1% iron oxide, into its furnace and adjust the temperature of the furnace to 300° C. Connect the tube containing the nickel to the auxiliary tube by means of a section of 2-mm. bore capillary tubing equipped with ball joints at each end. Connect the exit end of the auxiliary tube to stopcock *E* by means of stainless steel hypodermic tubing fitted with metal ball joints. Seal the joints with sealing wax. Disconnect stopcock *F* from the hydrogen source and sweep the hydrogen from the rubber tubing by introducing carbon dioxide through stopcocks *G* and *F*. Sweep hydrogen from the absorption tower by passing carbon dioxide through stopcocks *G*, *F*, *E*, and *D*. Attach the rubber tubing to a source of cylinder oxygen; cylinder oxygen is used for oxidation of the tube packing because of the relatively small capacity of the electrolytic oxygen generator. Remove the cap from the fitting on the entrance end of the combustion tube and turn stopcocks *F* and *E* so that oxygen can be introduced into the combustion tube through the auxiliary furnace. Adjust the flow of oxygen to 10 ml. per minute and oxidize the nickel for a distance of 90 mm. Recap the front end of the tube and turn stopcocks *F*, *G*, and *E* so that oxygen flows into the entrance end of the combustion tube and into the absorption tower; leave stopcock *D* open to the atmosphere. Oxidize a 70-mm. section of the nickel, then slowly (to prevent surface oxidation of the nickel) sweep the tube with carbon dioxide. Disconnect the tubing from *F* and adjust the temperature of the main furnace to 1000° C. and that of the auxiliary furnace to 700° C. When not in use, keep the system filled with carbon dioxide and the furnaces at operating temperatures.

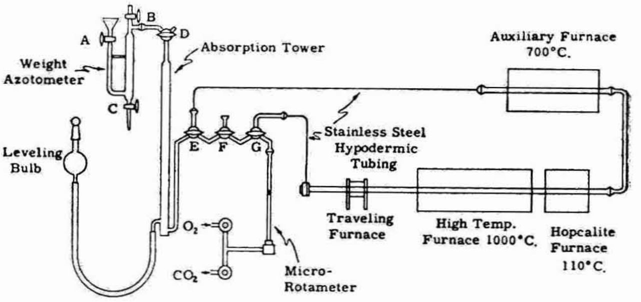

Figure 2. Gas Flow System for Micro-Dumas Apparatus

It is necessary to condition the newly installed high temperature combustion tube. This is accomplished by determining the nitrogen content of acetanilide, as described below, until a value is obtained which deviates from the true value by 0.1% nitrogen or less. Usually a satisfactory value is obtained after three or four analyses.

A quartz rod, approximately 5 cm. long and of such diameter as to fit into the combustion tube with a clearance of about 0.5 mm., is inserted into the tube behind the boat to prevent sample vapors from backing up and provide some conduction of heat to the boat in the early stages of pyrolysis. A loop drawn at one end of the quartz rod facilitates its removal from the combustion tube. A hook made from small-diameter brass rod is used to remove the boat and quartz plug from the tube.

Combustion Furnaces. The nickel–nickel oxide section of the high temperature combustion tube is heated to 1000° C. by means of a 23-cm. furnace wound with Kanthal (C. O. Jelliff Mfg. Co., Southport, Conn.) resistance wire. The furnace is controlled by means of a variable autotransformer and its temperature is indicated by a pyrometer. The hopcalite is heated by a furnace consisting of an insulated aluminum cylinder, 11 cm. in length, and drilled to accommodate three cartridge-type heaters, the tube, and a thermo-switch set to maintain the temperature at 110° C. The auxiliary tube containing precipitated copper oxide is maintained at 700° C. by a 13-cm. furnace wound with Chromel resistance wire and controlled by a variable autotransformer. The traveling furnace that is employed for vaporization of the sample consists of a 6-cm. length of Alundum tubing wound with platinum–10% rhodium resistance wire and is maintained at approximately 1000° C. during operation. The rate of travel of this furnace is determined by the voltage that is applied to the drive motor through a variable autotransformer.

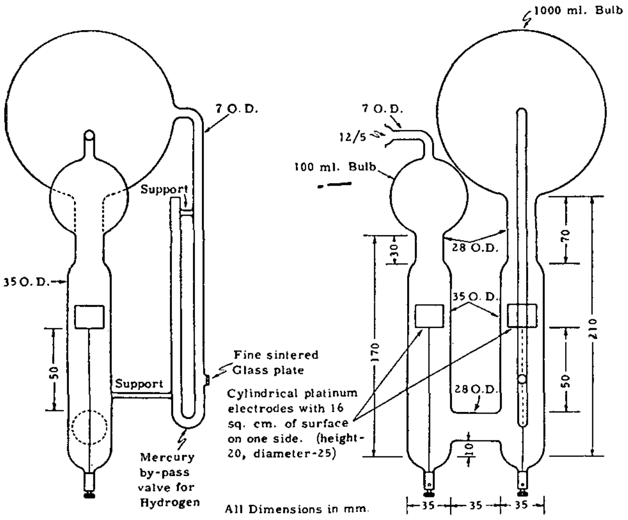

Figure 3. Electrolytic Oxygen Generator

Gas-Measuring System. The gas-measuring system consists of an ungraduated absorption tower filled with 30% potassium hydroxide solution and a weight azotometer filled with mercury. Sufficient mercury is placed in the bottom of the absorption tower to form a column extending 3 to 5 mm. above the inlet side arm; this prevents the caustic from draining out through the side arm. The combustion products are swept into the absorption tower by a stream of carbon dioxide. The caustic solution absorbs the carbon dioxide and the residual gas volume is measured by displacing and weighing an equal volume of mercury as described by Koch *et al.* (*7*).

PROCEDURE

Before making the first analysis of the day, purge the carbon dioxide and oxygen lines by venting the gases to the atmosphere through stopcock *F*. Determine whether any air is entering the apparatus as follows: Open stopcock *D* to the atmosphere and raise the leveling bulb until the potassium hydroxide solution rises to the mark etched on the capillary portion of the absorption tower. Mark the position of the leveling bulb so that it can be returned to this position. Close stopcock *D* and lower the leveling bulb. Pass 60 ml. of carbon dioxide at a rate of 10 ml. per minute through stopcock *G*, the combustion tubes, stopcock *E*, and into the absorption tower. Open stockcock *D* to the atmosphere and return the level of potassium hydroxide solution to the mark. Close stopcock *D*, lower the leveling bulb, and again pass 60 ml. of carbon dioxide into the absorption tower at a rate of 10 ml. per minute. Close stopcocks *A*, *B*, and *E* and raise the leveling bulb to the previously fixed upper position. Turn stopcock *D* to connect the absorption tower to the weight azotometer and, by means of stopcock *C*, drain mercury into a small weighed weighing bottle until the level of potassium hydroxide solution returns to the mark. Weigh the mercury; the amount displaced should be less than 0.1 gram.

Blank Determination. Open stopcock *D* to the atmosphere and bring the level of potassium hydroxide solution to the mark. Close stopcock *D* and turn *E* to communicate the absorption tower to the combustion tubes. Lower the leveling bulb and pass carbon dioxide through the apparatus and into the absorption tower for 17 minutes at a rate of 3 ml. per minute. Change the gas flow to oxygen and pass oxygen through the tube for 6 minutes at a rate of 5 ml. per minute. Follow with carbon dioxide at a rate of 5 ml. per minute for 4 minutes.

Increase the rate of flow of carbon dioxide to 10 ml. per minute and maintain this flow for 5 minutes. Open stopcocks *A* and *B* to the atmosphere for a few seconds and determine the residual gas volume by displacing mercury as above. Less than 0.2 gram of mercury should be displaced.

Analysis of Sample. Bring the level of potassium hydroxide solution to the mark, close stopcock *D*, and lower the leveling bulb. Accurately weigh sufficient sample to yield 0.5 to 2.0 mg. of nitrogen, but do not take more than 25 mg. in any case. Weigh solids and nonvolatile liquids in platinum boats. Weigh hygroscopic samples in boats enclosed in glass piggies. Draw volatile samples into weighed glass capillary tubes with a bulb in the middle (*1*). Seal one end of the sample tube, weigh the capillary plus sample, and quickly dip the open end into melted paraffin. Place the capillary on a platinum tray before putting it into the combustion tube.

Place a quantity of solid carbon dioxide over that section of the combustion tube which contains the sample. Open the front end of the combustion tube and pass carbon dioxide through stopcocks *G*, *F*, and *E* and out the front end of the combustion tube at the rate of 40 ml. per minute. Insert the sample and push the sample to within 5 or 6 cm. of the high temperature furnace with the hook. Insert the quartz plug so that it touches the boat and replace the cap on the front end of the combustion tube; screw the cap on firmly. Quickly turn stopcocks *G* and *E* so that carbon dioxide flows through the combustion tubes and into the absorption tower. Reduce the flow of carbon dioxide to 10 ml. per minute and maintain this flow for 6 minutes. Open stopcock *D* to the atmosphere and allow the potassium hydroxide solution to flow into the leveling bulb. Bring the level of potassium hydroxide to the mark on the capillary as before. Close stopcock *D* and pass 60 ml. of carbon dioxide through the tube and measure the residual gas as described; repeat if more than 0.1 gram of mercury is obtained. Continued high values indicate that the sample is vaporizing or the system is leaking.

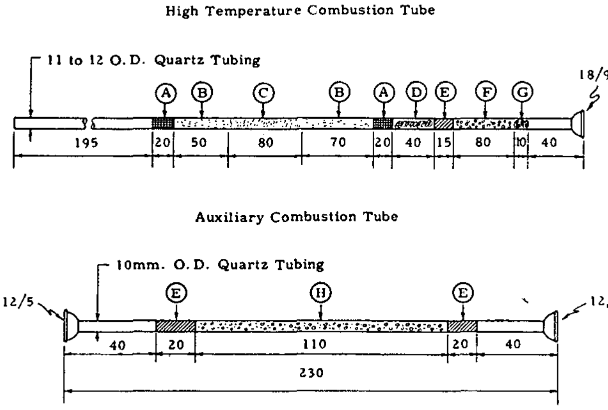

Figure 4. Quartz Combustion Tubes and Packings

A. **60-mesh nickel gauze**
B. **150-mesh oxidized nickel powder**
C. **150-mesh nickel powder**
D. **Quartz wool**
E. **40-mesh copper gauze**
F. **Hopcalite**
G. **Glass wool**
H. **Precipitated copper oxide plus iron oxide**
All dimensions in millimeters

Open stopcock *D* and return the level of the potassium hydroxide solution to the mark. Close stopcock *D*, lower the leveling bulb, turn on the carbon dioxide, and adjust the flow of carbon dioxide to 3 ml. per minute. Remove the solid carbon dioxide from around the combustion tube and turn on the heater of the traveling furnace. Move the furnace to within 1 to 2 cm. of the sample and allow it to warm up for about 2 minutes. Start the furnace traveling by increasing the drive motor voltage with the variable autotransformer. Adjust the rate of travel so that the sample is burned slowly and at a uniform rate, as indicated by the rate of formation and size of the gas bubbles in the absorption tower. Conduct the combustion at such a rate that the traveling furnace reaches the high temperature furnace in less than 17 minutes. When a total of 17 minutes has elapsed from the time the travel of the furnace was started, return the traveling furnace to a position directly over the sample. Turn off the carbon dioxide, turn on the oxygen, and adjust its flow to 5 ml. per minute. After 2 minutes has elapsed, start the furnace traveling at such a rate that it will reach the high temperature furnace in 4 minutes. Turn off the oxygen and pass carbon dioxide through the tube for 4 minutes at a rate of 5 ml. per minute, then for 5 minutes at a rate of 10 ml. per minute. Turn off the carbon dioxide and the heater of the traveling furnace and close stopcock *E*. Momentarily open stopcocks *A* and *B* to the atmosphere, place the leveling bulb in its upper position and open stopcock *D* to the weight azotometer. Displace mercury into the weighing bottle through stopcock *C* until the level of the caustic solution returns to the mark on the capillary. Weigh the mercury to the nearest 0.005 gram.

DISCUSSION

The method described has been routinely applied to a wide variety of materials over a period of several years. The method permits an operator to complete five or six analyses per 8-hour working day and the compact, rugged design of the apparatus minimizes the maintenance work that is required. Results typical of those obtained are shown in Table I. The pooled standard deviation of replicate tests from their average is 0.05%. Appropriate statistical tests failed to show the presence of systematic errors, thus indicating that the results are not significantly influenced by the type of nitrogen compound tested. Single results should not differ from the theoretical value by more than 0.11% for more than one time in 20. If duplicate tests are made, the average should not differ from the theoretical value by more than 0.08% for more than one time in 20.

The practice in this laboratory at one time was to use a combustion tube packed with copper and copper oxide in a manner similar to that described by Pregl; both copper gauze and wire-form copper oxide were used. The temperature of the first oxidized portion of the filling was maintained at 900° C., since at this temperature it was found that methane was quantitatively oxidized with a contact time of approximately 15 seconds. At lower temperatures such as are commonly used in micro-Dumas combustions, a much longer contact time was required. However, it was found that the copper–copper oxide filling was not completely adequate for dinitro compounds; such compounds gave nitrogen values which generally were about 0.5% low. A solution to this problem was presented by Kirsten (*4*), who obtained excellent results for such materials by employing a nickel–nickel oxide filling maintained at 1000° C. At this temperature some carbon dioxide dissociated to form carbon monoxide, causing positive errors, so part of the tube was packed with hopcalite to reoxidize the carbon monoxide. Kirsten used nickelous oxide and nickel for the tube filling. He prepared the nickel by reducing the oxide with hydrogen at an unstated temperature. In attempting to repeat his work, nickelous oxide was reduced with hydrogen at 800° C. in the combustion tube, but the filling fused into a mass of hard lumps. At 550° to 600° C. reduction was effected without this difficulty; however, a shrinkage of about 50% took place during reduction. Further tests showed that the use of 150-mesh nickel powder (A. D. Mackay, 198 Broadway, New York 7, N. Y.) as the starting material circumvented this difficulty; this material also proved to be more convenient to handle.

Theoretical nitrogen results were obtained when the nickel–nickel oxide packing was used for the analysis of a variety of materials; however, petroleum fractions consistently yielded results which were high by as much as 1% nitrogen. This was attributed to the formation and incomplete combustion of methane. The difficulty was overcome by passing the gases from the combustion tube through an auxiliary tube maintained at 700° C. and packed with precipitated copper oxide containing 1% ferric oxide (*8*). This modification resulted in a marked improvement; however, the low but consistently positive values obtained for nitrogen-free hydrocarbons (Table I) may be the result of incomplete oxidation of methane. The simpler expedient of Kirsten (*5*), who employed a tube with an enlarged nickel–nickel oxide catalyst zone, proved to be inadequate in the authors' hands. Possibly the nickel oxide was not so active as that prepared by Kirsten. It seemed that the apparatus could be simplified by using the precipitated copper oxide containing iron oxide to oxidize both methane and carbon monoxide, thus eliminating the hopcalite packing and furnace. However, tests showed that incomplete combustion of the carbon monoxide was obtained with this catalyst under the conditions employed.

Kirsten (*6*) points out that nitrogen oxides are retained by nickel oxide when free oxygen is present in the combustion tube. On the basis of this observation the use of oxygen to burn carbonaceous residues would appear to offer a source of error. However, since oxygen is introduced after the sample has been pyrolyzed, the chance of oxides of nitrogen and oxygen being present together in the combustion tube is small.

Table I. Application of Micro-Dumas Method to Various Materials

Material	Approximate Sample Wt., Mg.	Nitrogen, % Theory	Nitrogen, % Found	Nitrogen, % Dev. from theory
Acetanilide	7.5	10.36	10.36	0.00
	6.6	...	10.32	−0.04
Acridine	6.6	7.82	7.80	−0.02
	6.2	...	7.83	+0.01
Azobenzene	10.7	15.38	15.29	−0.09
	7.9	...	15.48	+0.10
	8.4	...	15.39	+0.01
	7.1	...	15.37	−0.01
s-Benzylisothiourea hydrochloride	7.0	...	13.78	−0.04
	6.7	13.82	13.69	−0.13
	7.9	...	13.81	−0.01
	8.2	...	13.67	−0.15
p-Chloroacetanilide	8.3	8.26	8.24	−0.02
	8.7	...	8.21	−0.05
Cystine	8.6	11.66	11.55	−0.11
	7.3	...	11.60	−0.06
	8.7	...	11.57	−0.09
2,4-Dinitropheno	9.9	15.22	15.30	+0.08
	7.3	...	15.30	+0.08
	7.1	...	15.20	−0.02
	7.4	...	15.26	+0.04
Gasoline	8.4	0.00	0.06	+0.06
	13.1	...	0.04	+0.04
n-Heptane	11.7	0.00	0.06	+0.06
p-Iodoacetanilide	12.7	5.37	5.40	+0.03
	9.2	...	5.45	+0.08
	9.1	...	5.49	+0.12
	11.6	...	5.44	+0.07
Nicotinic acid	9.6	11.38	11.37	−0.01
	8.5	...	11.40	+0.02
p-Nitrophenol	7.2	10.07	10.08	+0.01
	9.1	...	10.14	+0.07
	9.9	...	9.98	−0.09
	10.8	...	10.05	−0.02
White oil	16.3	0.00	0.08	+0.08
	12.2	...	0.03	+0.03
	14.1	...	0.01	+0.01
	14.4	...	0.10	+0.10
	11.7	...	0.05	+0.05
n,*n*-Diisopropyl bibutane phosphinic amide	9.9	5.36	5.39	+0.03
	10.2	...	5.30	−0.06
Quinoline	13.0	10.85	10.85	0.00
	14.2	...	10.91	+0.06

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Quantitative Determination of S-35–Labeled Compounds In Complex Mixtures

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IN THE determination of the radioactivity of solid samples which emit weak beta particles, it is necessary to consider the absorption of radioactivity by the precipitate itself. Studies of this problem have been carried out with compounds of carbon-14 (*1*) and sulfur-35 (*3*). Useful methods for correction of such data for absorption have been presented by Yankwich *et al.* (*7*). In general, the final step in the preparation of samples consists of conversion to a single pure substance such as carbonate or sulfate, followed by precipitation in a standard manner as an insoluble substance.

In many metabolic experiments employing tracer techniques, it is possible to isolate the labeled species from all other labeled substances without purifying it. Thus one may have a single labeled amino acid in a solution containing an unknown mixture of tissue components as well as inorganic salts. At this point it is tempting to carry out the radioactive determination by evaporating the mixture in a planchet and counting directly.

Hogness *et al.* (*4*) have described this procedure for use with biological fluids of relatively constant composition, in which case an absorption curve can be prepared for each set of conditions. The absorption is not necessarily simply a function of the total weight of the sample when this method is used. Serious errors can occur if the curve prepared under one set of conditions is used to interpret data collected under other conditions, such as a change in a buffer or other alteration in the make-up of the medium used.

This report concerns an attempt to find a simple procedure for the direct comparison of radioactivity in heterogeneous mixtures containing a single radioactive substance, but avoiding the necessity of preparing a correction curve for each change in variable. The method adopted is a modification of one suggested by Leslie [described by Calvin *et al.* (*1*, page 107)], and consists of using a piece of paper in the bottom of the planchet in which the evaporation occurs. With this method it is possible to prepare a master curve for the correction of observed radioactivity as a function of total weight of sample added to the paper, and still stay within the limits of error allowable in many metabolic experiments.

METHODS

All the results reported here were obtained with a sample of S-35–labeled DL-methionine, specific activity the order of 19 millicuries per gram, which was obtained from D. L. Tabern of the Abbott Laboratories. About 10^{-3} millimole of methionine was used as the labeled addendum in the following measurements, and the activity of this in absence of any other addition was considered to be 100% under the conditions used in each case. Radioactivity determinations were made with a proportional counter and scaler, using an internal counter tube filled with methane. All samples were counted for a sufficient time to record 1000 counts over the background. Two methods were used in preparing samples for the determination of counting rate.

Method A. The samples were evaporated to dryness at room temperature in aluminum planchets of 3.6-cm. diameter. The radioactive amino acid and other substances were added as suitable aliquots of stock solutions, and the final volume was adjusted so that the original depth was the same in all planchets.

Method B. The samples were prepared as described above. However, the planchets were constructed of Parafilm (Grade M, obtainable from the Marathon Corp., Menasha, Wis.) by pinching the corners to make a plastic dish 3 cm. square. The bottom of this dish was lined with a square of Whatman No. 1 filter paper, which weighed about 100 mg. Up to 2 ml. of liquid can be placed in such planchets conveniently.

RESULTS

Some preliminary experiments were carried out in which the solution was evaporated to dryness on a piece of paper hanging in the air. This procedure has been used for carbon-11 determinations by Ruben *et al.* (*6*) and has also been used for carbon-14 (*5*). It is dangerous unless particular precautions are taken to control the rate of evaporation. When a fan or lamp was used to speed evaporation, differences of over 100% were observed in the counting rate of the two sides of the paper. Hence this procedure has been abandoned as impractical for routine work.

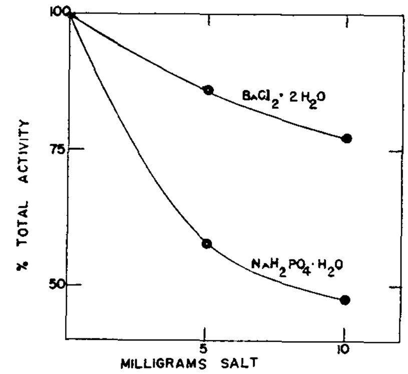

Figure 1. Effect of Inert Additions on Counting Rate of S-35–Labeled Methionine

Samples prepared by evaporation on aluminum planchets (Method A). Each point represents average of 10 separate samples

Absorption Curves for Method A. With this procedure absorption curves were run using barium chloride and sodium phosphate as inert additions. It is obvious from the curves obtained (Figure 1) that the corrections to be applied to the observed counting rate depend upon the nature of the absorbent as well as the total weight of samples. This is shown also by curve 2 of Figure 2, the self-absorption curve for methionine, which is unlike either of the curves of Figure 1. This serves to emphasize the necessity for preparing a correction curve for each set of conditions if data obtained by direct evaporation of heterogeneous samples are to be interpreted correctly.

Self-Absorption. The self-absorption by methionine was found to be different for the two methods, as is evident from the curves in Figure 2. Addition of methionine when the filter paper was present (Method B) had no effect other than a slight increase in counting rate until over 5 mg. of methionine had been added. Above this point the absorption followed a curve similar to that observed when the solution was evaporated in the absence of paper (Method A). It is significant that in all the samples containing 10 mg. or more of methionine, crystals of the compound were clearly visible on the top of the paper. Thus it is concluded that the observed counting rate of samples prepared by Method B is essentially independent of the specific activity of the sample as long as conditions are maintained which preclude the formation of crystals on top of the paper.

Absorption Curves for Method B. Substances other than the radioactive substance itself exerted a definite effect on the counting rate, which appeared to decrease logarithmically as the total weight increased. An absorption curve for a number of samples prepared with varying amounts of monosodium phosphate is shown in Figure 3. In Figure 4 the effect of a wide variety of materials on the counting rate is shown. The mean deviation of these points from the phosphate curve is 3.7%. It is evident that the effect of a given weight of these substances on the counting rate of samples prepared by Method B is relatively constant.

Table I. Effect of Cupric Ion on Counting Rate of Samples Prepared by Method B

(Each value represents average of 10 determinations)

Additions	Mg.	% Total Activity
$CuCl_2.2H_2O$	9	82.0
Glycine	6	87.3
$CuCl_2.2H_2O$ + Glycine	9 6	
Calculated[a]		69.3
Observed		83.0
$CuCl_2.2H_2O$ + HCl	9 0.1 meq.	90.0

[a] Calculated on assumption that effects of cupric chloride and glycine are additive.

Effect of Complex Formation. The effect of cupric ion, known to form complexes with amino acids (*2*), was investigated. The data presented in Figure 5 indicate anomalous behavior in the presence of copper. It seems likely that the complex formation alters the distribution of the methionine in the paper. This is further emphasized by the data in Table I, where the effect of the cupric ion is reversed by adding an excess of glycine to compete for the copper ion, or by making the solution acid, which reduces complex formation. Both treatments brought the counting rate up to that expected on the basis of Figure 4.

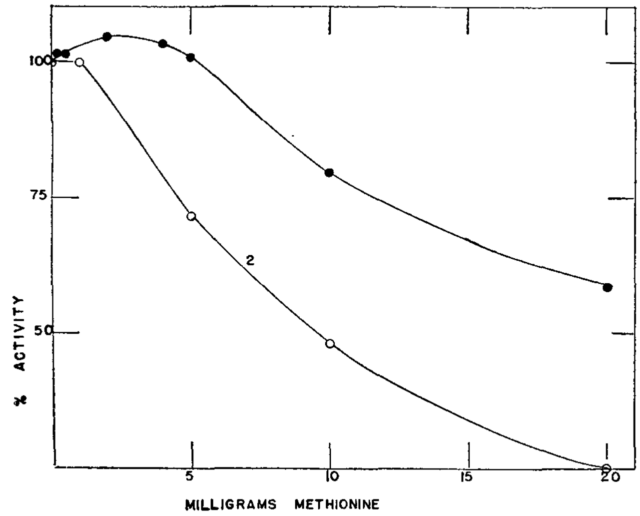

Figure 2. Self-Absorption Curves for Methionine

1. Samples prepared by evaporation in plastic planchets lined with filter paper (Method B) 2. Samples evaporated in aluminum planchets (Method A). Each point represents average of 10 samples

Table II. Effect of Area of Paper on Counting Rate of Samples Prepared by Method B

(Each value represents an average of ten determinations)

Area, Square Inches	Counts per Minute
1.56	1051
0.56	1356
0.14	1825

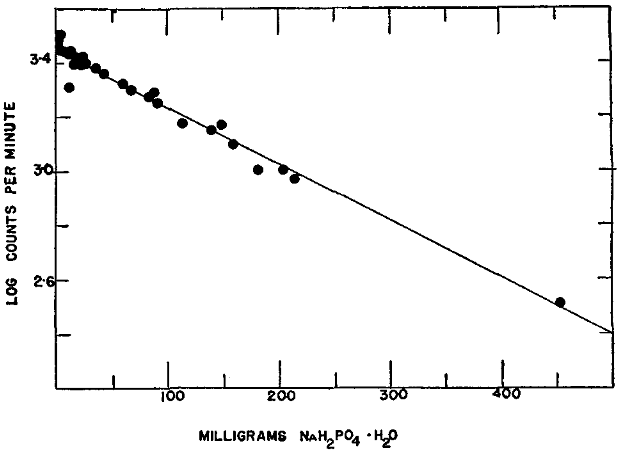

Figure 3. Effect of Sodium Phosphate on Counting Rate of S-35 Methionine

Samples prepared by evaporation in plastic planchets lined with filter paper (Method B)

Effect of Area of Paper. In these experiments samples were prepared by Method B, but the area of the plastic planchet was altered. In each case an identical amount of methionine was added. Water was added to the larger planchets so that the depth of the liquid was the same in each planchet at the outset. The data presented in Table II show the observed counting rate to increase as the planchet size is diminished. However, a decrease of over tenfold in the size of the paper is seen to increase the counting rate by less than a factor of 2. Thus the limits of paper area are wide for all practical purposes.

Effect of Total Activity. The observed counting rate of samples prepared by Method B is linear with respect to the actual number of disintegrations. This is shown in Table III, where the amount of labeled methionine was varied over a factor of 10.

DISCUSSION

The reason for the logarithmic relationship shown in Figure 3 is not clear, as there is evidence that the distribution in the paper is not uniform. In general, if the papers are lifted out of the planchets and counted, the upper side is about 10% more active. In one experiment five identical sheets of paper were stacked in a planchet in place of the usual single sheet and counted separately

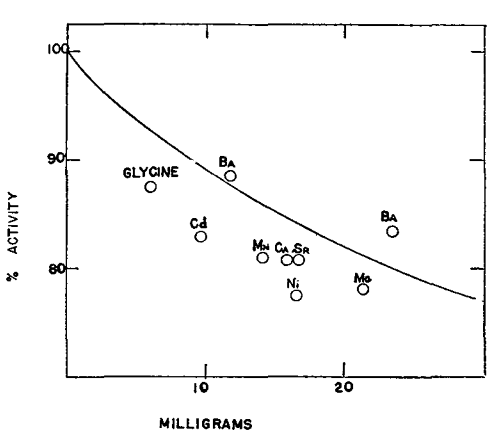

Figure 4. Effect of Additions on Counting Rate of Samples Prepared by Method B

Smooth curve taken from data on $NaH_2PO_4.H_2O$. Each point is average of 10 samples. Milligram axis refers to total weight of solids. Forms present were: $BaCl_2.2H_2O$, $CaCl_2.3H_2O$, $MnCl_2.3H_2O$, $SrCl_2.6H_2O$, $CdCl_2$, $MgCl_2.6H_2O$, and $NiCl_2.6H_2O$

Table III. Effect of Total Activity

S-35-Labeled Methionine, Micromole	Counts/Min.	Observed Specific Activity, Counts/ Min./Micromole
0.0176	2925	166
0.00878	1243	142
0.00351	580	165
0.00176	275	156

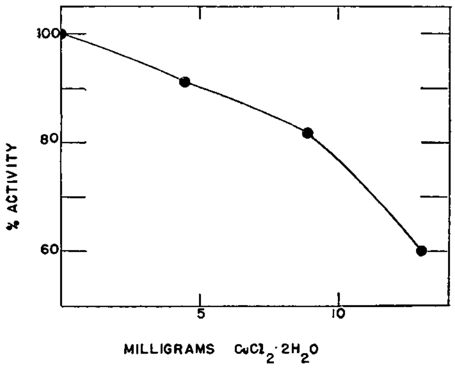

Figure 5. Effect of Copper on Counting Rate of Samples Prepared by Method B

Each point is average of 10 samples

after drying in the usual manner. In this case the counting rate for the upper side of the sheets, starting with the top one, was 747, 192, 121, 131, and 380 counts per minute, respectively. Although this procedure introduced the additional variable of a series of interfaces between the sheets, the results serve to indicate that the active species moves both up and down through the paper as evaporation proceeds. It would seem that the equations derived by Henriques *et al.* for solid precipitates do not apply to this process (*3*). Presumably the actual rate of movement depends on a variety of factors, including temperature. It is significant that when water was added to samples and permitted to re-evaporate under the same conditions, no marked effect on the counting rate was observed.

In spite of the complexity of the process leading to the distribution of the labeled substance in the paper, the precision obtained is at least as great as that observed with direct evaporation on planchets. The standard error for a mean calculated from triplicate determinations is less than 4% by either method. This compares favorably with the precision obtained after the more tedious procedure involving conversion to barium or benzidine sulfate (*3*), particularly as such methods require at least two additional transfers of small amounts of materials.

The less desirable features of this method of sample preparation include the absorption of radiation by the paper. The counting rate of samples prepared by Method B was approximately 20% of that observed with identical samples prepared by Method A. The availability of compounds of high specific activity makes this loss permissible in many procedures. It is also obvious that the independence of counting rate and specific activity can introduce errors if large amounts of the labeled species are present and the total weight of sample is not suitably corrected. Finally, any factor, such as complex formation, which alters the movement of the labeled species through the paper, can lead to erroneous results. In practice, these sources of error can be generally avoided in designing the experiment.

The chief advantage is the relatively small and constant alteration in counting rate introduced by other components of the mixture in which the radioactivity is to be determined. The changes in absorbers tested represent more drastic changes than would normally occur in practice. This would seem to make this a satisfactory method for the direct comparison of radioactivity in heterogeneous mixtures.

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Determination of Nitro Nitrogen by the Kjeldahl Method

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THE Kjeldahl method (*4*) is not applicable to every form of organic nitrogen. However, owing to the comparative ease of operation, many attempts have been made to generalize the method.

Treatment of nitro compounds with phenols to convert them into a more easily reducible form was first suggested by Jodlbauer (*3*). Later, Cope (*2*) substituted salicylic acid for phenol. Complete recovery of the nitrogen in nitro and other so-called refractory compounds is not always accomplished by the use of these, even in conjunction with sodium thiosulfate.

The generally accepted procedure for nitro compounds uses 5 grams of sodium thiosulfate and 10 grams of potassium sulfate as a boiling point raiser. The severity of this reaction is increased by using larger amounts of potassium sulfate, which has been shown by other investigators (*5, 6*). Using *p*-dinitrobenzene as a typical compound whose nitrogen is not readily available, it was determined that 18 grams of potassium sulfate was the optimum (see Table I).

EFFECT OF INCREASED DIGESTION TEMPERATURES

To demonstrate the difference between the use of the conventional 10 grams of potassium sulfate and 18 grams, a number of compounds were compared using the following procedure:

Weigh into a Kjeldahl flask 0.1 to 0.15 gram of sample and 35 ml. of concentrated sulfuric acid containing 1 gram of salicylic acid. Let stand for 0.5 hour on the steam bath, or until the sample has completely dissolved. Transfer to the digestion rack and add 5 grams of sodium thiosulfate. Let stand for 0.5 hour and then heat gently until the mixture carbonizes. Cool and add potassium sulfate and 0.25 gram of mixed catalyst (*1*), ($FeSO_4.7H_2O$–Se). Heat strongly until the mixture clears, and boil gently for 1 hour. Cool, dilute with distilled water, and determine the nitrogen in the usual manner.

Table I. *p*-Dinitrobenzene

(Calculated 16.68%)

K_2SO_4 Added, Grams	Nitrogen, %	K_2SO_4 Added, Grams	Nitrogen, %
2	15.01	14	15.49
4	15.04	16	15.30
6	15.19	18	16.27
8	15.23	20	15.11[a]
10	15.18	22	15.20[a]
12	15.47	24	15.48[a]

[a] Pasty digest on cooling.

Table II. Effect of Increasing Potassium Sulfate to 18 Grams

	Nitrogen, %[b]		
Compound[a]	K_2SO_4, 10 grams	K_2SO_4, 18 grams	Calcd.
o-Dinitrobenzene	12.98	14.48	16.68
m-Dinitrobenzene	16.66	16.67	16.68
p-Dinitrobenzene	15.15	15.49	16.68
m-Nitrochlorobenzene	6.17	6.76	8.89
p-Nitrochlorobenzene	6.61	8.07	8.89
2,5-Dichloronitrobenzene	2.40	4.58	7.30
3,4-Dichloronitrobenzene	3.82	5.57	7.30
2,4-Dinitroaniline	...	22.01	22.95
2,4-Dinitrophenol	13.90	14.00	15.22
2,4-Dinitroresorcinol	14.70	15.46	15.38
3,5-Dinitrobenzoic acid	12.28	12.62	13.21
3-Nitrosalicylic acid	6.89	7.07	7.65
5-Nitrosalicylic acid	7.06	7.31	7.65

[a] Eastman Kodak Co. highest purity or equivalent.
[b] Average of two determinations.

From Table II, it will be seen that while the results do not reach the calculated percentage, in most cases there has been an appreciable gain owing to the larger amount of sulfate used and the consequent increase of digestion temperature.

EFFECT OF HYDROXY COMPOUNDS ON CONVERSION OF NITRO GROUPS

Because phenol and salicylic acid, both hydroxy compounds, apparently help in the conversion of nitro groups, it was believed that other aromatic hydroxy compounds might have a similar effect. The following procedure was used, the salicylic acid being replaced in the same amount by the various hydroxy compounds. *o*- and *p*-Dinitrobenzene, typical refractory compounds, were used.

Procedure. Weigh into a Kjeldahl flask 0.10 to 0.15 gram of sample and add 35 ml. of concentrated sulfuric acid containing 1 gram of the hydroxy compound (or combination). Let stand for 0.5 hour on the steam bath, or until the sample has completely dissolved. Transfer to the digestion rack and add 5 grams of sodium thiosulfate. Let stand for 0.5 hour, then heat gently until the mixture carbonizes. Cool, and add 18 grams of potassium sulfate and 0.25 gram of mixed catalyst ($FeSO_4.7H_2O$-Se). Heat strongly until the mixture clears, and boil gently for 1 hour. Cool, dilute with distilled water, and determine nitrogen in the usual manner.

The results (Table III) show that the most suitable combination is a mixture of equal parts of 1-naphthol and pyrogallol. Further determinations were made on a number of compounds using the above procedure with 1-naphthol–pyrogallol. A comparison of results is shown in Table IV. In some cases, the calculated amount of nitrogen has been reached; in every case an increase is noted over the results found by the use of the conventional salicylic acid.

In a recent paper, McCutchan *et al.* (7) have suggested the use of thiosalicylic acid. Comparative results using this and 1-naphthol–pyrogallol are shown in Table V. For the compounds analyzed, the method using 1-naphthol–pyrogallol, in most cases, gives somewhat higher results.

CONCLUSIONS

The data presented indicate that the use of 1-naphthol–pyrogallol tends to give better results than salicylic acid on the compounds analyzed. A comparison of this procedure and the procedure using thiosalicylic acid shows some improvement over the latter.

Table III. Effect of Aromatic Hydroxy Compounds on *o*- and *p*-Dinitrobenzene

Concd. H_2SO_4, 1 Gram/35 Ml.	*o*-Dinitrobenzene, 16.68% *N*	*p*-Dinitrobenzene, 16.68% *N*
Salicylic acid	14.48	15.49
1-Naphthol	15.09	16.03
2-Naphthol	14.95	15.88
Catechol	14.80	15.23
Resorcinol	14.00	15.49
Pyrogallol	15.63	16.00
Hydroquinone	15.12	14.77
Phloroglucinol	13.17	15.72
Gallic acid	15.65	15.76
Salicylic acid Pyrogallol 1:1	13.89	16.13
Salicylic acid Hydroquinone 1:1	14.88	15.09
Gallic acid Pyrogallol 1:1	15.90	15.89
Gallic acid 1-Naphthol 1:1	15.69	15.79
Pyrogallol 1-Naphthol 1:1	15.95	16.28
Pyrogallol 2-Naphthol 1:1	15.77	15.38

Table IV. Comparison of Results Using Salicylic Acid and 1-Naphthol–Pyrogallol

	Nitrogen[b], %		
Compound[a]	Salicylic acid	1-Naphthol–pyrogallol	Calcd.
o-Dinitrobenzene	14.48	16.15 16.02 15.95 16.33	16.68
p-Dinitrobenzene	15.49	16.28 16.62 16.22 16.47	16.68
m-Nitrochlorobenzene	6.76	7.84	8.89
p-Nitrochlorobenzene	8.07	8.80	8.89
2,5-Dichloronitrobenzene	4.58	6.64	7.30
3,4-Dichloronitrobenzene	5.57	6.81	7.30
2,4-Dinitroaniline	22.01	22.42	22.95
3,5-Dinitrobenzoic acid	12.62	13.26	13.21
3-Nitrosalicylic acid	7.07	7.69	7.65
5-Nitrosalicylic acid	7.31	7.65	7.65
2,6-Dichloro-4-nitrophenol	6.35	6.53	6.74

[a] Eastman Kodak Co. highest purity or equivalent.
[b] Average of two determinations.

Table V. Comparison of Results Using 1-Naphthol–Pyrogallol and Thiosalicylic Acid

	Nitrogen[b], %		
Compound[a]	1-Naphthol–pyrogallol	Thiosalicylic acid	Calcd.
p-Nitrochlorobenzene	8.80	8.42	8.89
2,4-Dinitrochlorobenzene	13.84	13.88	13.82
m-Dinitrobenzene	16.66	16.72	16.68
o-Nitrotoluene	10.60	8.73	10.22
Picrolonic acid	17.23	12.39	21.21
Azobenzene	15.36	15.33	15.38
Pyrrole	20.64	19.76	20.87
Piperine	4.63	4.30	4.69
Piperidine	12.09	10.56	14.43

[a] Eastman Kodak Co. highest purity or equivalent.
[b] Average of two determinations.

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Simplified Apparatus for Quantitative Hydrogenation

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THE fundamental characteristics of any apparatus for quantitative hydrogenation are given by Gatterman and Wieland (*1*) in a drawing which shows a reaction vessel connected mechanically to an agitating motor, and connected to a gas buret by means of a piece of flexible tubing. The buret is provided with a leveling bulb and has a separate connection to a source of hydrogen gas. Modifications of this basic design that have been described in the literature were made in order to eliminate sources of error which arise from the following three problems:

1. The apparatus must either be maintained at constant temperature and pressure, or corrections for changing ambient temperature and pressure must be made.
2. The sample must be brought into contact with the reduced catalyst and hydrogen without opening the apparatus to the air.
3. The mixture of sample, catalyst, solvent, and hydrogen must be vigorously agitated, but the agitation must not be conducive to the leakage of hydrogen.

The last problem is the most difficult.

Some of the hydrogenation assemblies that have been described in the literature are elaborate. A high-precision apparatus which gave results of less than 0.3% maximum deviation is reported by Vandenheuvel (*7*), who also presents an excellent discussion of the problems attendant upon rate studies of hydrogenation. The apparatus described in this paper is believed to approach the ultimate in simplicity and low cost, while retaining good accuracy.

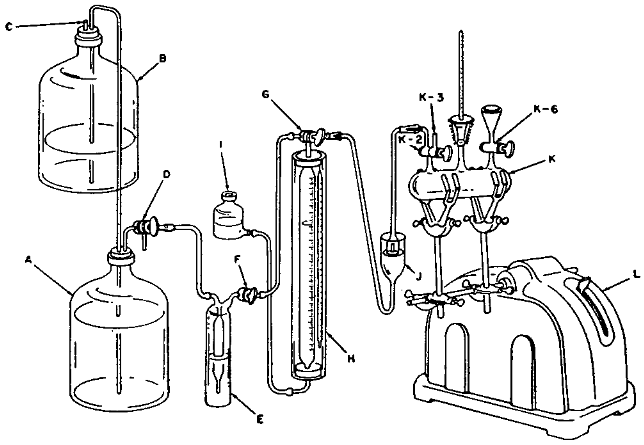

Figure 1. Hydrogenation Assembly

A. **Hydrogen storage bottle**
B. **Water reservoir bottle**
C. **Vent to atmosphere**
D. **3-Way stopcock**
E. **Purifying jar, Fleming type**
F. **Single-bore stopcock**
G. **3-Way stopcock**
H. **Gas-measuring unit, Technical Universal Model, Fisher No. 10-600-36 or equivalent. Unit modified by joining a 10/30 outer joint on right arm of stopcock *G***
I. **Leveling bottle**
J. **Flexible coupling. See Figure 2 for details**
K. **Reaction flask. See Figure 3 for details**
L. **Burrell shaker**

The determinations that were run in this laboratory with the apparatus shown in Figure 1 were made on the macro scale, with a consumption of from 2 to 10 millimoles of hydrogen, but it is probably possible to scale down the apparatus to semimicro dimensions, if a hydrogen consumption of the order of tenths of a millimole is desired.

PROVISIONS FOR AGITATION

A unique feature of the apparatus is the flexible coupling shown in detail in Figure 2, which allows for agitation of the reaction vessel, but provides a mercury seal against hydrogen leakage. The design also allows for absorption of minor surges of gas pressure.

The lower portion of the coupling, *J*-2 to *J*-5 inclusive, is stationary, and makes an all-glass connection with the buret. The upper portion of the coupling, *J*-6 and *J*-7, connects with the reaction flask, and moves in a small arc centered at *J*-1.

The reaction flask, Figure 3, is agitated by means of the Burrell Wrist-Action shaker, size B. The clamps furnished with the shaker are removed, and muffs and clamps suitable for holding the reaction flask parallel to and about 20 cm. above the shaft are substituted. The Burrell shaker has an adjustment for the amplitude of the shaking arc, so that it is an easy matter to adjust the agitation to the point where the mixture in the flask just "rolls" to the top of the flask and splashes back to the bottom. This type of agitation by shaking is thought to be more thorough and more free from dead spots than agitation by magnetic stirrers, both rotary (*4*, *6*) and oscillatory (*7*, *8*). Agitation by shaking has proved especially practical in this laboratory for the reactions of resins, which are often very viscous.

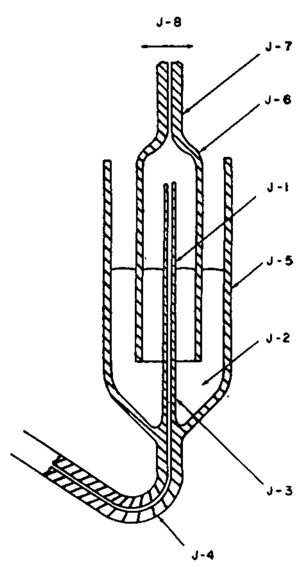

Figure 2. Flexible Coupling

***J*-1.** **Center of shaft of shaker, and level of mercury**
***J*-2.** **Mercury**
***J*-3.** **3-mm. o.d. standard wall tubing**
***J*-4.** **1-mm. i.d. 7-mm. o.d. capillary tubing**
***J*-5.** **35-mm. o.d. standard wall tubing**
***J*-6.** **18-mm. o.d. standard-wall tubing**
J-7. **1-mm i.d., 7-mm. o.d. capillary tubing**
***J*-8.** **Arc through which upper portion oscillates about *J*-1 as center**

Attempts to make a leakproof, flexible coupling by means of rubber or plastic tubing were unsuccessful. The lowest rate of hydrogen leakage that was obtained in the apparatus employing flexible tubing was 0.08 cc. per hour. This is in marked contrast with the results obtained with the mercury-sealed flexible coupling, which gave no detectable leakage in 24 hours on a blank run conducted with hydrogen and solvent only in the reaction flask.

Another means of avoiding hydrogen leakage is to eliminate the flexible coupling altogether by mounting the entire hydrogenation assembly on a board, and agitating the board as a unit (*2*, *3*, *5*). This system is highly adaptable to a semimicro apparatus, but would probably be too cumbersome for larger assemblies, or where more vigorous agitation is required.

At constant pressure, the hydrogenation reactions run in this laboratory conform closely to a first-order equation. Under these circumstances the importance of a leakproof apparatus becomes manifest, inasmuch as it is extremely difficult to distinguish hydrogen leakage from residual absorption of hydrogen by the unsaturated compound at the end of the reaction. The distinction can be made only if the reaction is run for a sufficiently long time to arrive at a constant rate of hydrogen uptake. A correction for leakage may then be made by running the apparatus for a prolonged time to establish the leakage rate and extrapolating back to zero reaction time, but the correction is uncertain and time-consuming.

APPARATUS

The assembly of the component parts of the apparatus is shown in Figure 1.

Flexible tubing connections are permissible in the train up to stopcock *G*, but subsequent joints must be all-glass. All stopcocks and ground-glass joints must be ground in thoroughly for a precise fit.

Five-gallon narrow-mouthed bottles, *A* and *B*, are used for hydrogen storage. Bottle *A* is filled with water to the stopper, and a tank of electrolytic-grade hydrogen is connected to the open tube of stopcock *D*. The air is flushed from the lines by appropriate manipulation of the stopcocks, and *A* is filled with hydrogen by displacing the water into bottle *B*. The purifying jar, *E*, contains concentrated sulfuric acid for removal of the water from the hydrogen.

Details of the reaction flask, *K*, are shown in Figure 3. The salient features are the funnel, *K*-7, for admitting catalyst, solvent, and sample to the flask (*4*), and the thermometer, *K*-9, for reading the internal temperature of the flask.

The buret, *H*, is the 100-cc. water-jacketed model with leveling bulb, common to many types of gas analysis apparatus. The water jacket is used as an air jacket, to stabilize the effect of changing room temperature. A thermometer is hung in the space between the buret and the air jacket. The leveling bulb, *I*, is filled with the solvent used for the sample in the determination. Glacial acetic acid has been very satisfactory for hydrogenations run in this laboratory.

PROCEDURE

The air is removed and the apparatus is filled with hydrogen by attaching a vacuum pump to tube *K*-3 of the reaction flask. The air is first removed from the buret by displacing it with acetic acid from the leveling bottle, and the buret is filled with hydrogen from the storage bottle. Stopcock *G* is left in the position connecting *F* and *J*. Stopcock *K*-6 is then closed and stopcock *K*-2 is turned to connect the flask with the vacuum pump. The various stopcocks are turned to give a continuous connection between the storage bottle and stopcock *K*-2. The reaction flask is evacuated to the full capacity of the pump, and hydrogen is then gradually admitted to the flask by careful manipulation of stopcock *K*-2. The evacuation and filling of the flask with hydrogen are repeated five times.

The catalyst is then inserted in funnel *K*-7 and rinsed into the flask with a pipetted amount of solvent. This is accomplished by appropriate manipulations of the leveling bottle and stopcocks *G* and *K*-6, rigorous care being taken that no air be admitted to the flask. Agitation is then started, and the reduction of the catalyst is permitted to go to completion.

At the completion of the reduction of the catalyst the initial readings are taken for calculation of the volume of hydrogen consumed in the determination. The leveling bulb is brought to the level in the buret, and the buret reading, the barometric pressure, and the temperatures of the buret and the reaction flask, given by the respective thermometers, and read and recorded.

The sample is then inserted in the funnel of the reaction flask and rinsed in with pipetted portions of solvent, using the same technique as in the addition of catalyst. It is convenient to use an aliquot of a sample weighed into a volumetric flask. An accurate record of the volume of liquid in the reaction flask must be kept. The agitation is started and the reduction of the sample is permitted to proceed. Additions of hydrogen may be made as necessary by stopping the agitation, closing stopcocks *G* and *K*-2, and adding hydrogen from the storage bottle through stopcock *G*, recording the initial and final buret volumes at atmospheric pressure and the buret temperature for each addition.

When the reaction is completed readings are taken for the buret volume and temperature, the flask temperature, and the barometric pressure, in the same manner as for the initial reading. Both stopcocks of the reaction flask are closed, the flask is removed from the assembly, and as a safety measure the hydrogen in the flask is flushed out with a mild current of nitrogen before exposing the residual contents to the atmosphere.

CALCULATIONS

Corrections for varying atmospheric temperature and pressure are made by reducing all volumes to standard conditions of temperature and pressure before calculating the hydrogen consumed. The volume of hydrogen consumed will be equal to the initial volume in the buret, tubing, and reaction flask, plus the volume added from the storage bottle during the hydrogenation, minus the volume in the buret, tubing, and flask at the end of the reaction. The hydrogen will be saturated with solvent vapor at all times, so that the vapor pressure of the solvent at the temperature of the volume being read must be subtracted from the atmospheric pressure; the resulting partial pressure will then be the hydrogen pressure which is used in converting to standard temperature and pressure. The reduction to standard temperature and pressure for the gas in the buret is performed separately from that for the gas in the reaction flask and tubing, because the two thermometers are seldom at the same temperature. The volume of gas in the tubing between the buret and the flask is comparatively small, and is added to the volume in the flask for the reduction to standard temperature and pressure. The gas volume in the buret is obtained from the buret reading, and the gas volume in the flask is the gross volume of the flask minus the liquid volume; this liquid volume will be the volume of solvent used to wash in the catalyst for the initial reading, and the sum of the catalyst washings, sample volume, and sample washings, for the final reading. The gross volume of the flask and tubing is conveniently obtained with sufficient accuracy by measuring the quantity of liquid required to fill the flask and by calculating the volume of tubing from measurements of the diameter and length of the various sections. The calculation of the net volume of hydrogen consumed at standard temperature and pressure is made in accordance with the method of Johns and Seiferle (*3*), who describe the computations in detail, and give an example.

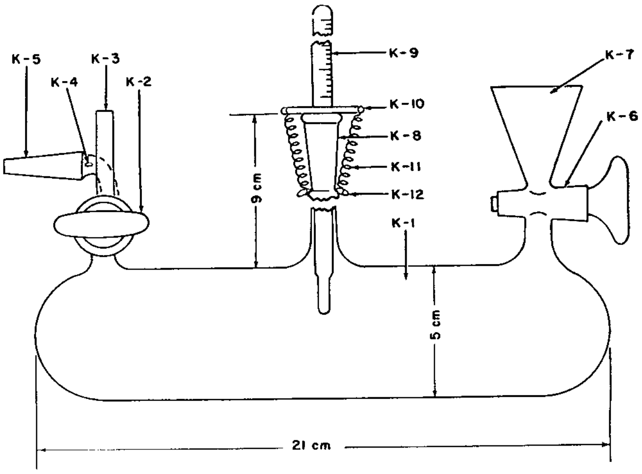

Figure 3. Reaction Flask

K- 1.	**Body of flask, 50-mm., standard wall borosilicate glass tubing**
K- 2.	**3-way stopcock, two outlets on one side**
K- 3.	**Outlet for connection to vacuum pump**
K- 4.	**Hooks for retaining springs**
K- 5.	**10/30 inner joint**
K- 6.	**Single-bore stopcock**
K- 7.	**Funnel, conical, about 10-ml. capacity, 35 × 35 mm.**
K- 8.	**10/30 outer joint**
K- 9.	**Thermometer with 10/30 joint, 77-mm. immersion, −10° to 110° C.**
K-10.	**Metal plate for holding thermometer in place**
K-11.	**Retaining springs**
K-12.	**Hooks for retaining springs**

RESULTS

The estimated standard deviation for a single determination was determined from a series of duplicate determinations on 21 lots of three varieties of unsaturated resins. The series of determinations was performed by three independent operators. The over-all estimated standard deviation was 0.88%. The maximum deviation from the mean was 1.14%, and the minimum deviation was 0.03%, for a 140-cc. volume of hydrogen consumed.

Satisfactory checks with the theoretical values were obtained for esters of various unsaturated acids using the hydrogen as received, without further purification. A purification train for the removal of oxygen is described by Prater and Haagen-Smit (*5*).

CATALYSIS

A 0.1-gram quantity of platinic oxide was used successfully with various acrylic, maleic, and fumaric esters. The reaction was usually 99% complete, or more, in 1 hour of agitation, 3 hours being allowed for the determination. For the hydrogenation of maleic anhydride and viscous polyesters a satisfactory rate of reaction was obtained with a more dispersed catalyst, 10% palladium on activated charcoal powder. Both catalysts were made by Baker & Co., Inc.

Hydrogenations which are somewhat too slow for practical analytical purposes may be accelerated by heating the reaction flask slightly. A convenient means of applying heat is to wind electrical heating tape around the reaction flask. A successful reaction was carried out in this manner at 80° C. The flask was cooled to room temperature for volume readings.

ACKNOWLEDGMENT

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Mechanism of High-Frequency Titration

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THIS paper is a contribution to the study of the theoretical aspects of high-frequency titration. Results have been obtained with apparatus capable of giving the necessary data, to explain the response of a high-frequency analysis apparatus, where the solution vessel is placed in the coil of the tank circuit. In addition to the regions of sensitivity recently given by others, the apparatus and method described reveal an additional region of sensitivity in the range 0.1 to 1.0*N* (for hydrochloric acid) not previously reported.

The apparatus is unique in that it uses a modulated resonance frequency source and an "infinite-impedance" detector followed by an audio-amplifier and a vacuum-tube voltmeter. The solution to be studied is placed in a glass vessel in the coil of a tuned circuit and the voltmeter output is plotted as a function of the dial setting of the resonance frequency source. For each solution so studied there are obtained the frequency of maximum resonance and the magnitude of the output at maximum resonance. The sensitivity characteristics of the instrument are then obtained by plotting the resonance frequency and the maximum output at resonance as a function of concentration for various electrolytes.

Recently several studies (*1, 6, 18*) have gone far toward explaining the results of high-frequency titrations on a sound theoretical basis. These studies were all based upon apparatus in which the solutions studied were placed in capacitor-type cells.

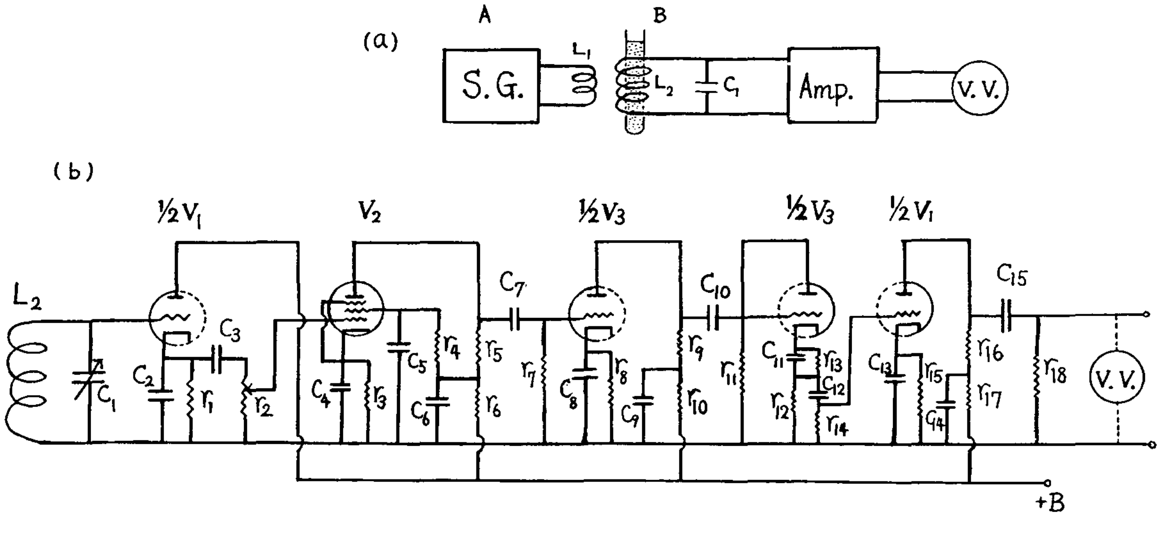

Figure 1. Schematic Diagram of Apparatus

C_1.	460 μf.	C_{10}, C_{15}.	0.05 μf.	r_9, r_{11}, r_{12}, r_{16}.	50 Kw.
C_2.	100 μf.	r_1, r_{18}.	100 Kw.	r_{10}, r_{17}.	20 Kw.
C_3, C_{12}.	0.01 μf.	r_2, r_7, r_{14}.	500 Kw.	r_{13}.	1 Kw.
C_4, C_8, C_{13}.	10 μf.	r_3.	1 Kw.	V_1.	6SN7
C_5, C_{11}.	0.1 μf.	r_4, r_5.	250 Kw.	V_2.	6SJ7
C_6, C_9, C_{14}.	6 μf.	r_6.	30 Kw.	V_3.	6SN7
C_7.	0.005 μf.	r_8, r_{15}.	1 Kw.	*V.V.*	Tube voltmeter

The object of this paper is to present the results of an attempt, with apparatus capable of giving the necessary data, to explain the response of a high-frequency analysis apparatus where the solution vessel is placed in the coil of the tank circuit. This study reveals a region of sensitivity in a higher concentration region than any previously reported.

APPARATUS AND METHOD

In order to analyze the response of high-frequency titration data, at least two factors must be measured at the same time. Accordingly, an apparatus has been constructed in order to observe precisely the resonance frequency and a voltage proportional to the resonant voltage of the tank circuit where the solution vessel is placed in the coil.

Figure 1*a* shows a block diagram of the complete apparatus and Figure 1*b* shows a circuit diagram of the tank circuit, detector, and amplifier. Radio waves of approximately 2.54 or 5.98 Mc. modulated at 1000 cycles are produced by an Oki No. 102 signal generator. These are fed to the detector circuit (L_2, C_1, 1/2 6SN7) through the electromagnetic coupling between L_1 and L_2. Coils L_1 and L_2 are made of copper tubing 6 mm. in diameter. The coils have, respectively, 6 and 14 turns, and their diameter is 100 mm. The coils are maintained about 5 cm. apart. The Q-value of the circuit is maintained very high by the "infinite impedance" detector circuit. After amplification by the 6SJ7 and 6SN7 tubes, the output voltage is measured by a vacuum-tube voltmeter. The solution to be studied is placed in a glass tube 50 mm. in diameter and 250 mm. long, which is placed in coil L_2. The coils, detector circuit, and amplifier are completely shielded. The surface of the solution lies 35 mm. above the shielding box. At 2.54 Mc., when the glass tube is empty, or when it is filled with 250 ml. of distilled water, the Q-value of the tuned circuit is 318.

The measurement of the Q-value of circuit L_2 and C_1 containing the solution is carried out as follows. The vessel containing 350 ml. of a solution is placed in coil L_2. The tuning condenser, C_1, is fixed to tune L_2 and C_1 to the frequency of the experiment, say 2.54 Mc., and remains fixed throughout the remainder of the experiment. The output voltage is measured by the vacuum-tube voltmeter. The frequency of the signal generator is changed by about 4 kc. (one scale division of the calibrated dial) and the output is measured each time the frequency is changed. The resonance curve is obtained by plotting the signal generator dial reading as abscissa and the vacuum-tube voltmeter readings as ordinate.

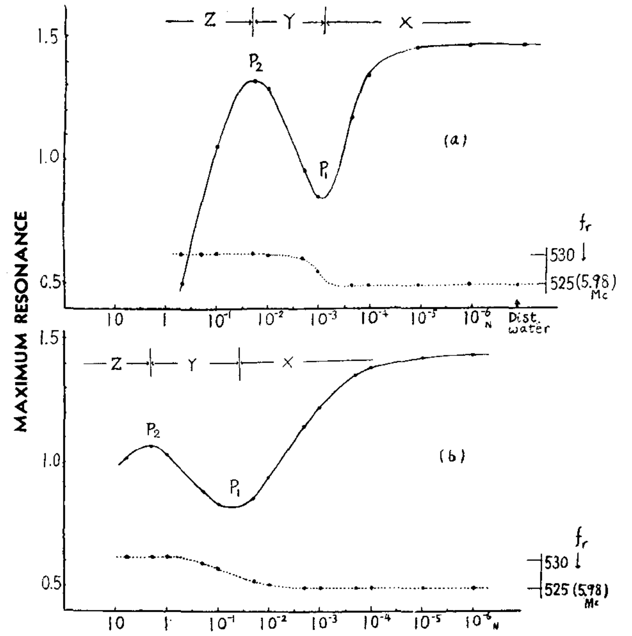

Figure 3. Relation of Maximum Resonance to Concentration

a. Hydrochloric acid
b. Acetic acid

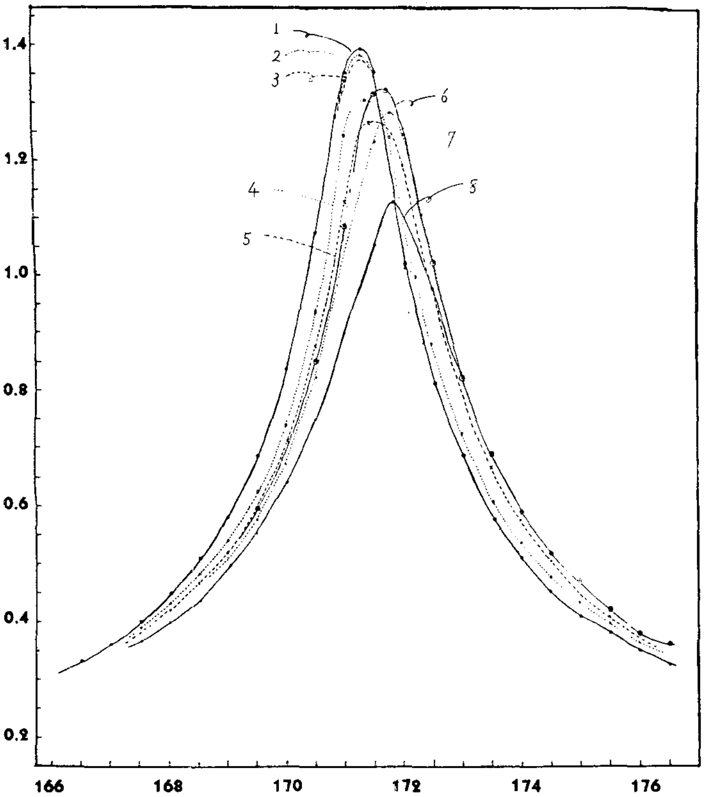

Figure 2. Resonance Curves of Circuits Containing Solutions of Hydrochloric Acid of Following Concentrations (*N*)

1. 0 (distilled water)
2. 10^{-6}
3. 10^{-5}
4. 10^{-4}
5. 10^{-3}
6. 2×10^{-3}
7. 2×10^{-2}
8. 10^{-1}

In Figure 2 are plotted curves for several different concentrations of hydrochloric acid. The maximum point of each curve represents the resonance frequency and the magnitude of the maximum resonance for each solution.

EXPERIMENTAL RESULTS

According to Figure 2, the resonance frequency changes only slightly with concentration, but the magnitude of maximum resonance changes rather markedly. In Figure 3 the maximum resonance voltage and the resonance frequency are plotted as a function of the concentration of the solution for hydrochloric acid and for acetic acid. These data are for 5.98 Mc. For the purpose of discussion, these curves may be divided into three regions, *X*, *Y*, and *Z*, separated by one minimum point, P_1, and one maximum point, P_2, as shown in Figure 3. Similar curves were obtained for hydrochloric acid, sodium chloride, and sodium hydroxide at 2.54 Mc., except that the minimum, P_1, is less pronounced (Figure 4).

In region *X*, the resonant maximum increases as the concentration of the solution decreases, and finally attains the value of distilled water. In region *Y*, the resonant maximum increases with increase of concentration to the maximum at P_2. As the concentration becomes still greater, the value of the resonant maximum decreases rapidly. As it

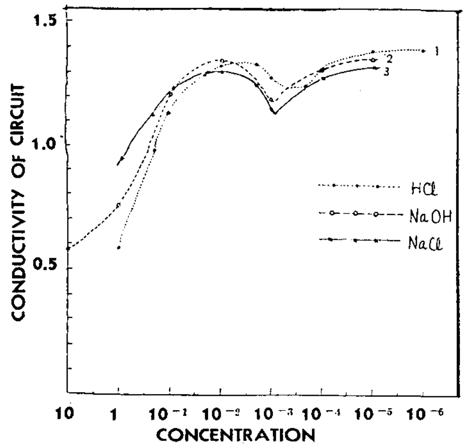

Figure 4. Relation of Maximum Resonance to Concentration

Experiment carried out at 2.54 Mc.

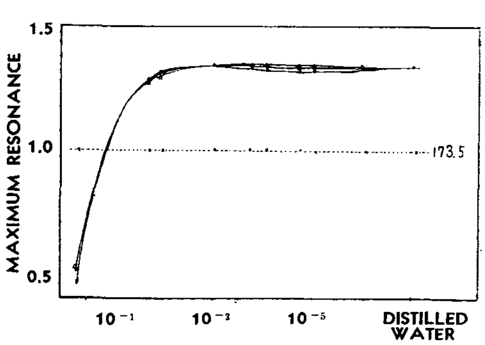

Figure 5. Relation of Concentration to Maximum Resonance

Solid line
a. 2 ml.
b. 4 ml.
c. 6 ml.
$1N$ solutions of sodium chloride coexisting with hydrochloric acid
Dashed line
x. Curve for resonance frequency
Experiments carried out at 2.54 Mc.

may be assumed that changes in resonance frequency are due principally to changes in inductance or capacitance of the tuned circuit, and changes in the value of maximum resonance are due to changes in resistive loading, it may be concluded from the data shown in Figure 3 that resistive changes are significant at both higher and lower concentrations than are capacitive or inductive changes.

Experiments were carried out in which 2, 4, and 6 ml. of $1N$ sodium chloride were added to the water in the glass vessel before addition of the hydrochloric acid was begun. These data are shown in Figure 5, and indicate the elimination of the variations in the X and Y branches of the curve, but the variation in the region Z is retained. As regions X and Y are the most sensitive regions for titration, it is not desirable to add ions or salts not participating in the reaction.

As has been shown previously (*1*, *6*, *18*), there are great differences between the acid-base titration curves of solutions having different concentrations. Figure 6 shows the results of titrations with the apparatus described here at several different concentrations of acid and base. In Figure 6, curve *a* is in the part of sensitivity region X where little change of resonant voltage or frequency should be expected. Curve *b* is in the part of region X where the sensitivity is good, and since the slope of the curve of Figure 3 is positive in this region the resonant value at the end point is a maximum. Curve *c* is in the region Y where sensitivity is good, and since the slope of the curve of Figure 3 is negative in this region, the resonant value at the end point is a minimum. Curve *d* is in sensitivity region Z. This region of rather good sensitivity for this apparatus occurs in a relatively high concentration of electrolyte. Because of the logarithmic concentration plot of Figure 3, this sensitivity is not so great as might at first be thought, but this region of sensitivity has not been mentioned in any previous publications.

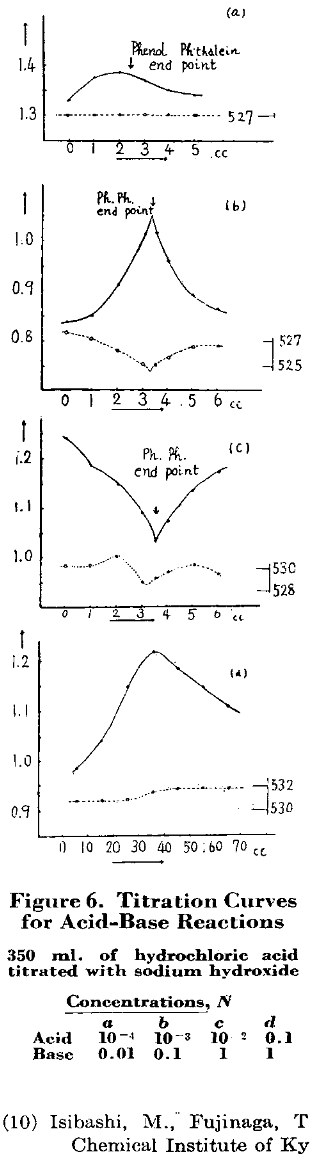

Figure 6. Titration Curves for Acid-Base Reactions

350 ml. of hydrochloric acid titrated with sodium hydroxide

	Concentrations, *N*			
	a	*b*	*c*	*d*
Acid	10^{-4}	10^{-3}	10^{-2}	0.1
Base	0.01	0.1	1	1

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Assay of Radioiron and Radiosilver in Biological Samples

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IN THE course of experiments on the metabolism of radiosilver, silver-110, in rats, it was necessary to correct the radiosilver concentration, expressed as activity per gram of dry weight of tissue, for the activity contributed by the blood of that tissue. This information was obtained indirectly by transfusing blood containing erythrocytes tagged with radioiron, iron-55, from a donor rat into the rat containing silver-110 according to the technique previously described (*7*). Since each tissue contained both silver-110 and iron-55, it was necessary to devise a method which would permit their activities to be measured independently of each other. This was accomplished by separating the two elements using the cupferron extraction procedure (*1, 4–6*).

REAGENTS

α,α -Bipyridine, 0.1% aqueous solution.

Cupferron (ammonium salt of nitrosophenylhydroxylamine, G. Frederick Smith Chemical Co., Columbus, Ohio), 6% aqueous solution. Prepare a fresh solution daily and keep in refrigerator until used.

Silver-110 nitrate ($Ag^{110}NO_3$), specific activity 15 mc. per gram of silver; 5.7×10^{-4} mg. of silver per ml.

Carrier iron solution, 1 mg. of iron per ml. Dissolve, with warming, chemically pure iron wire in a few milliliters of concentrated nitric acid and hydrochloric acid and dilute to volume. This is referred to as the "carrier iron" solution.

Iron-55 ammonium citrate, specific activity 258×10^{-3} mc. per mg. of iron; 311×10^{-6} mg. of (ferric) iron per ml.

Iron-59 ammonium citrate, specific activity 64×10^{-3} mc. per mg. of iron; 42×10^{-6} mg. of (ferric) iron per ml.

APPARATUS FOR COUNTING

All gamma-activity measurements were made by means of a scintillation counter and standard scaler. The detector consisted of a tellurium activated–sodium iodide crystal (Harshaw Chemical Co., Cleveland, Ohio) coupled to an RCA 5819 photomultiplier tube. The signals from the photomultiplier were coupled directly to a standard scaling circuit having a 0.25-volt threshold.

Each gamma-activity measurement was made on a 5-ml. portion of the solution contained in a 5-ml. capacity vial. High counting efficiency was attained, as the vial just fitted into a circular well in the crystal $^5/_8$ inch in diameter and 1.5 inches in depth. No increase in counting rate above background was detected when the scintillation counter was exposed to the 5.9 k.e.v. x-rays from iron-55.

The activity of the electroplated iron-55 was measured with an argon-filled G-M tube (Tracerlab, Boston, Mass.).

ELECTROPLATING PROCEDURE AND EQUIPMENT

The electroplating procedure and equipment were essentially those previously described (*3*). Electroplating was carried out from a saturated aqueous ammonium oxalate solution at an initial pH of 5 to 6 at 6 volts, 0.5 ampere. Plating was considered complete when the plating solution contained 1γ (0.35%) or less of iron per ml. of plating solution. The iron was estimated with bipyridine (*3*), except that ascorbic acid was substituted for sodium bisulfite since it yielded more reproducible results.

DIGESTION OF TISSUES

All tissues, the largest of which weighed less than 10 grams, were wet-ashed. The tissue was placed in a 300-ml. Kjeldahl flask together with 10 mg. of carrier iron and sulfuric acid and heated until fuming occurred. Two milliliters of concentrated sulfuric acid were used for the first 3 grams and 1 ml. for each additional gram. After fuming occurred, 30% hydrogen peroxide was added, 1 to 2 drops at a time, until all organic matter was destroyed. Since salts tend to crystallize out of cold concentrated sulfuric acid, thus making transfer of the digest difficult, 25 ml. of water were added and the flask was reheated until the volume was reduced to about 15 ml. The solution was then transferred to a 50-ml. graduated cylinder using three 5-ml. portions of 0.1*N* sulfuric acid for that purpose. The final volume was between 25 and 30 ml.

SEPARATION OF IRON-55 AND SILVER-110 BY CUPFERRON EXTRACTION

The digest was diluted to approximately 5*N* in a separatory funnel and cold freshly prepared cupferron solution and chloroform were added. One milliliter of cupferron per 10 ml. of digest and 10 ml. of chloroform were used. The mixture was shaken for about 30 seconds and the chloroform was removed. The aqueous phase was extracted twice more, using each time 5 ml. of chloroform. The entire extraction procedure was repeated after addition of 0.5 ml. of cupferron. All the iron was considered extracted when addition of 0.5 ml. of cupferron produced only a white turbidity.

The combined chloroform extracts were washed three times using each time 20 ml. of 3.6*N* sulfuric acid.

TESTS FOR RECOVERY OF IRON-55 AND SILVER-110

Recovery of Silver-110 from Rat Liver Digest. Seven milliliters of silver-110 nitrate having an activity of 110×10^3 counts per minute were added to a rat liver digest containing 7 ml. of concentrated sulfuric acid and 10 mg. of carrier iron. The solution was diluted to 5*N* and was extracted twice with cupferron.

The combined chloroform extracts, totaling 40 ml., were washed three times with 20-ml. portions of 3.6*N* sulfuric acid. The activity of each washing measured:

Washing No.	Volume of Washing, Ml.	Activity of Washing, C.P.M.	Added $Ag^{110}NO_3$, %
1	20	3460	3.2
2	20	360	0.3
3	20	120	0.09

The chloroform in the washed extract was evaporated on a steam bath and the cupferron was oxidized by heating with 2 ml. of concentrated sulfuric and nitric acids, respectively. The residual silver-110 activity of the digest was found to be 52 counts per minute or 4.7×10^{-2} % of the original activity.

Recovery of Iron-59 from Synthetic Mixture. To test the completeness of extractions of iron by cupferron, a mixture consisting of 0.8 ml. of iron-59 ammonium citrate, having an activity of 16×10^3 counts per minute, 10 mg. of carrier iron, and 3.5 ml. of concentrated sulfuric acid was heated to fuming and then diluted to 25 ml. The solution was extracted with chloroform after each of two additions of cupferron. The extracts were combined, the chloroform was evaporated, and the residue was oxidized with concentrated sulfuric and nitric acids. The gamma activity of the residue was found to be 15,680 counts per minute or 97.7% of the original activity.

Recovery of Iron-59 from Rat Liver Digest. Iron ammonium citrate (16,440 counts per minute) was mixed with 10 mg. of carrier iron and the digest obtained from a 10-gram rat liver; 16,200 counts per minute or 98.5% of the added activity was recovered in the washed chloroform extract.

Iron-59, a gamma emitter, was used in the above experiments because of the simplicity of its measurement in the absence of interfering silver-110.

From the above data it is apparent that iron and silver can be quantitatively separated from each other by means of extraction with cupferron, provided the chloroform extract is washed with an acid solution.

RECOVERY OF SILVER-110 AND IRON-55 FROM BIOLOGICAL SAMPLES

Various activities of iron-55 and silver-110 were mixed with rat tissues in the amounts usually present in unknown samples. After 10 mg. of carrier iron were added, the tissues were oxidized, the digests were transferred to separatory funnels, and the iron was extracted with cupferron. The chloroform extract was washed three times with 20-ml. portions of 3.6*N* sulfuric acid and the washings were added to the aqueous phase.

Table I. Recovery of Ag^{110} and Fe^{55} from Rat Tissues

Tissue		Ag^{110}			Fe^{55}	
	Wet wt., grams	Activity[a] added, c.p.m.	Recovered after cupferron extraction, %	Gamma Activity of Recovered Radioiron, C.P.M.	Activity added[b], c.p.m.	Recovered, %
Spleen	0.543	23,500	102	7	480	98
Kidney	2.32	11,700	97	8	720	97
Heart	0.868	2,350	102	9	240	100
Lung	1.43	4,700	99	8	480	98
Brain	1.02	2,350	97	8	240	104
Blood	2.0 (ml.)	11,700	98	7[c]	960	102
Liver	9.31	93,800	100	8	1440	92

[a] Specific activity: 4.4×10^7 c.p.m./mg. of silver.

[b] Specific activity: 154×10^5 c.p.m./mg. of iron.

[c] Gamma activity recovered before precipitation of ferric hydroxide from cupferrate digest.

Table II. Per Cent of Ag^{110} Electroplated in Presence of 10 Mg. of Inactive Iron[a]

Plating			Ag^{110}		
Voltage	Current, amp.	Time, hours	Gamma activity added[b], c.p.m.	Beta activity recovered[c], c.p.m.	Beta activity plated, %
9	0.5	5	11,900	900	73
9	0.5	5	11,900	910	73
6	0.3	1	15,200	176	11
6	0.3	2	15,200	166	10
6	0.3	3	15,200	275	17
6	0.3	4	15,200	170	11
4	0.02	4	8,675	100	11
4	0.02	4	9,750	115	11

[a] Each sample to be electroplated consisted of 10 mg. of inactive iron dissolved in 1 to 2 ml. of 6*N* sulfuric acid to which was added the indicated activity of $Ag^{110}NO_3$.

[b] Specific activity: 3.5×10^7 c.p.m./mg. of silver.

[c] Ratio of gamma activity, as measured in scintillation counter, to beta activity, as measured after electroplating with GM counter of duplicate amounts of activity, was 9.6 to 1.

As indicated in Table I, the recovery of silver-110 was essentially complete.

The chloroform was evaporated from the extract on a steam bath and the residue was wet-ashed with 5 ml. of concentrated sulfuric acid. The digest was transferred to a 100-ml. centrifuge tube and concentrated ammonium hydroxide was added until a brown precipitate, $Fe(OH)_3$, appeared. The suspension was centrifuged and the supernatant was discarded after being tested for iron as described under the plating procedure above. The precipitate was dissolved in 1 ml. of 6*N* sulfuric acid and was transferred to a 5-ml. capacity counting vial. The volume was made up to 5 ml. and the gamma activity was measured.

The gamma activity of the cupferrate digest obtained from blood was measured before rather than after precipitation of the ferric hydroxide in order to obtain an estimate of the loss in silver-110 gamma activity resulting from the precipitation procedure. The data (Table I, fifth column) indicate that less than 10 counts per minute, equivalent to 6×10^{-4} γ of silver, was present in each sample irrespective of whether or not the iron was precipitated before counting.

While destruction of the cupferrate permits more efficient transfer of the iron, the degradation products obtained tend to interfere with the electroplating of iron. These degradation products, however, remain in the supernatant and are discarded when the iron is precipitated as the hydroxide.

After the residual gamma activity of each radioiron sample was measured, the sample was transferred to an electroplating cell and the iron was plated out at 6 volts. The recovery of radioiron is listed in the last column of Table I.

Silver is plated out less efficiently, in the presence of 10 mg. of iron, at 6 volts than at 9 volts (Table II). No advantage is gained by reducing the voltage below 6 volts, as there is no further reduction in silver plating, while iron plating is markedly prolonged as a result of the reduced current density.

Consideration was given to differential counting of mixtures of either iron-59 or iron-55 and silver-110 in the liquid or solid state.

Silver-110, $\tau_{1/2}$ 270 days, has a complex decay process (*2*); its beta rays vary in maximum energy from 0.087 to 2.86 m.e.v. while emitting gammas from 0.116 to 1.516 m.e.v. Iron-59, $\tau_{1/2}$ 47 days, emits 0.46 and 0.26 m.e.v. maximum energy betas and 1.1 and 1.3 m.e.v. gammas. Iron-55, $\tau_{1/2}$ 2.91 years, decays by *K*-capture resulting in the emission of 5.9 k.e.v. x-rays.

Differential counting of silver-110 and iron-59 in solution based on differences in gamma-ray energy requires the use of a gamma-ray spectrometer. Such an instrument is not ordinarily available in most biochemical laboratories. Also, separation by chemical means of these two isotopes would result in preparations in which the degree of contamination of the one isotope by the other could not be ascertained.

Quantitative electroplating of either mixture of the two isotopes for the purpose of differential (*a*) beta counting in the case of silver-110 and iron-59 or (*b*) beta x-ray counting in the case of silver-110 and iron-55 would still require the removal of calcium and phosphates, as these substances interfere with electroplating.

Iron-55 was selected because it not only permits measurement of silver activity completely independently of the iron activity but also allows an estimate of the degree of contamination of the iron by the silver.

Separation of iron from silver by precipitation as ferric hydroxide, $Fe(OH)_3$, was considered. This method was found to be efficient for iron precipitation, but the precipitate always included an appreciable amount of silver activity. Furthermore, iron cannot be quantitatively precipitated in the presence of phosphates. The precipitation of silver chloride in acid solution would also yield no advantage, as calcium and phosphates are soluble under these conditions.

The cupferron extraction procedure was recently reported to yield extracts free of substances that interfere with the electroplating of iron (*4*). Although cupferron is known to extract elements other than iron (*1*), the above experiments demonstrate that it does not combine with silver under the conditions employed.

CONCLUSIONS

The cupferron extraction procedure has been applied to the separation of 10 mg. of iron containing a low iron-55 activity from as much as 2.13×10^{-3} mg. of silver containing a high activity of silver-110. The same extraction process also leaves calcium and phosphate, found in biological specimens, in the silver-containing fraction, thus permitting efficient electroplating of the iron-55. The use of iron-55 rather than iron-59 permits a check to be made on the efficiency of the separation of the silver from the iron in each sample.

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Addition Agents in Analytical Precipitations

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AN ADDITION agent may be defined as a substance added in small amount to a medium of precipitation to bring about a change in the physical characteristics of the substance precipitated. Addition agents have been employed widely for many years in electroplating processes, but only in isolated instances in chemical precipitation processes.

Buckley (*3*) and others have conducted thorough investigations of the modifications of crystal habit brought about by addition agents, particularly those that are organic dyes. Some addition agents have been employed as coagulating agents in gravimetric analysis. Orlow (*5*) proposed precipitating a known amount of aluminum oxide with barium sulfate to aid in coagulation of the precipitate, and Bogan and Moyer (*2*) reported that the coagulation of barium sulfate in the presence of excess barium ion is speeded by the addition of a small amount of agar-agar after the initial precipitation.

Table I. Substances Tested as Addition Agents in Precipitation Processes

Acetamide
Acetanilide
Aminotoluenesulfonic acid (1, 2, 5)
Benzenedisulfonic acid (*m*)
Benzyl isothiourea hydrochloride
2-Naphthol
Carbon disulfide
Chloral hydrate
Citric acid
Cresol
Disodium ethylenediamine tetraacetate dihydrate (Versene)
Ferric chloride
Formaldehyde
Glue
Goulac
Guanidine nitrate
Hydroxybenzaldehyde (*p*)
Naphthalenesulfonic acid
Naphthalenedisulfonic acid (1, 5)
Naphthol sodium disulfonate
Naphthol yellow S
Nitrophenol (*p*)
Oxalic acid
Phenylphenol (*o*)
Phenyl thiourea
Phthalic anhydride
Picric acid
Potassium bromate
Potassium dichromate
Potassium permanganate
Resorcinol
Saccharin
Sodium formate
Sodium peroxide
Sodium thiosulfate
Sulfanilamide
Sulfanilic acid
Tartaric acid
Thiophene
Thiosemicarbazide
Thiourea
Urea

Lindsly (*4*) demonstrated that picric acid, when present in the medium of precipitation, results in crystals of barium sulfate that are decidedly larger than those obtained without picric acid; this was definitely an alteration of crystal size and not merely a change in coagulating properties of the precipitate. Crystal size is of much importance in gravimetric analysis, from the standpoints of necessary digestion time, ease of filtration and washing, and surface coprecipitation of impurities.

The present study was undertaken to determine the effects of a wide variety of addition agents upon the size, shape, degree of perfection, and other characteristics of crystals of typical analytical precipitates. Three widely different precipitation processes were employed: the precipitation of barium sulfate, a crystalline precipitate which has been subjected to numerous investigations of other types; the precipitation of silver chloride, a curdy substance; and the precipitation of nickel dimethylglyoxime, a crystalline metallo-organic substance.

EXPERIMENTAL PROCEDURES AND DATA

The various substances tested as addition agents are listed in Table I. Each one was obtained as a U. S. Pharmacopeia, C.P., or reagent grade chemical, except those which were commercial products of indefinite composition. Each addition agent was tested in four concentrations: 0.005*M*, 0.001*M*, 0.0005*M*, and 0.0001*M*. A molecular weight of 200 was assumed arbitrarily for substances of indefinite composition.

In general, at least six replicate precipitations were conducted with each set of conditions for each size measurement. All six were observed qualitatively to ensure good reproducibility, then measurements were made on at least two of the six. Size measurements were made with an ocular micrometer on a light microscope. In each case the large crystals which formed were measured, and fragments and other fine, irregular material were disregarded. Thus, the size measurements indicate clearly the magnitude of the sizes and the trends in size variations. Numerous observations of shape and structure were also made with the electron microscope, although very little was added to the results of the observations with the light microscope.

Barium Sulfate Precipitations. Two distinct methods were employed in conducting the precipitation of barium sulfate. For survey studies of the effects of addition agents, the total volumes were kept small for convenience and reproducibility, although the volumes and concentrations were selected to represent aliquots of those ordinarily taken for analysis. Then quantitative determinations of sulfate were conducted with the aid of some of the addition agents with amounts of material directly equivalent to those normally used in analysis.

The experimental conditions employed for the survey studies of the effects of addition agents upon precipitated barium sulfate were as follows: 0.016*M* potassium sulfate solution; 0.020*M* barium chloride solution; pH of 1 for sulfate solution; temperature 60° C. for sulfate solution and 30° C. for barium chloride solution; reagents mixed by adding 2.5 ml. of barium chloride rapidly to 3.0 ml. of sulfate solution contained in a small vial; immediate gentle shaking by hand; other factors as listed in table of data. The barium chloride was added rapidly from a buret in some cases and rapidly by pouring in other cases; both methods yielded similar, reproducible, and homogeneous batches of crystals of barium sulfate. The rate and method of mixing were very critical from the standpoint of reproducibility of crystal size at higher temperatures, but not at the temperatures chosen. The relative amounts of the two reagents provide a 4% excess of barium ion, but this quantity was found not to be critical. After much preliminary work, it was found that the time of aging of the barium chloride solution with addition agent present prior to use was significant. Therefore this factor is listed in the table of data.

The major effect of addition agents upon the character of precipitated barium sulfate was upon the crystal size, both length and width. The shape and other general morphological characteristics remained unchanged with the various addition agents. Size data are presented in Table II for the effects of 0.005*M* addition agents in the barium chloride solution. The aging time listed represents the length of time which the barium chloride solution had been at room temperature after inserting the addition agent and before use in the precipitation tests. At addition agent concentrations of 0.001 and 0.0005*M*, the effects upon size were generally reduced in magnitude, but most of them were still appreciable. At 0.0001*M* concentrations of addition agent, some of the agents still exhibited appreciable influence, while others did not. Among those with considerable influence at concentration of 0.0001*M* were potassium permanganate, naphthol yellow S, and naphthalenesulfonic acid; while those no longer exhibiting any effect included cresol, picric acid, carbon disulfide, and ferric chloride. All addition agents not listed in Table II yielded sizes the same as those listed for no addition agent.

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Table II. Effect of 0.005M Addition Agents upon Crystal Size of Barium Sulfate

Addition Agent	Crystal Size as Function of Aging Time for Barium Chloride Solution Prior to Use					
	15 min.	1 hour	3 hours	6 hours	18 hours	24 hours
Benzenedisulfonic acid	7	11	36	56	90	100
Naphthalenesulfonic acid	9	14	27	50	90	100
Naphthalenedisulfonic acid	9	14	27	34	67	90
Naphthol yellow S	20	38	50	90	100	100
Cresol	9	14	14	16	20	30
Picric acid	9	14	20	27	45	75
Carbon disulfide	9	14	14	18	20	30
Benzyl isothiourea—HCl	9	16	27	31	40	50
Potassium permanganate	9	14	27	40	50	80
Ferric chloride	11	27	75	113	135	135
Thiosemicarbazide	7	9	14	14	40	70
Aminotoluene sulfonic acid	9	14	23	27	45	70
2-Naphthol	7	11	11	14	18	25
None	9	11	11	11	14	14

All measurements are in microns; all addition agents were added to the barium chloride solution and aged as indicated prior to use.

When the addition agent was added to the sulfate solution rather than to the barium chloride solution, no effects were observed except when very old barium chloride solution was used. In such cases the addition agents which exhibited the greatest increase in particle size when present in the barium chloride solution caused a slight increase in particle size. Further experiments revealed that results with barium nitrate solutions were the same as with barium chloride solutions.

Many experiments have been conducted in this laboratory to ascertain just what takes place in the barium chloride solution during the aging period, both with and without addition agents present. The only prior literature report of this phenomenon appears to be that of Bogan (*1*), who noted similar effects on simple barium chloride solutions, and suggested that the number of nuclei in the barium chloride solution may decrease with standing; he based this suggestion on the fact that he was able to obtain the same effect by filtering a fresh barium chloride solution through sintered glass of fine porosity. It is apparent that this aging effect is somehow related to the action of the addition agents.

Quantitative experiments were then conducted with three of the addition agents, picric acid, naphthalenedisulfonic acid, and potassium permanganate. Excess foreign ions were included in some of the tests to ascertain the influence of the agents upon the extent of coprecipitation. The results of the complete quantitative determinations revealed that the addition agents do not have any effect upon the accuracy of the determinations. Thus, the addition agents neither introduce any new error nor do they eliminate the usual coprecipitation errors. The precipitates exhibited no tendency to creep, and they settled out rapidly to leave clear supernatant liquid. Rapid filtration was accomplished with an easily handled precipitate and with no clogging of the filter medium.

Silver Chloride Precipitations. Again two distinct methods of precipitation were employed, one on a small scale for surveying the effects of addition agents and one on a larger scale for testing quantitatively those agents which appeared to be most effective.

The following is a summary of the experimental conditions employed in the survey experiments: 0.030M silver nitrate; 0.020M sodium chloride; pH of 6 for sodium chloride solution; temperature 30° C. for both reagent solutions; 2.2 ml. of silver nitrate solution added rapidly from a buret to 3.0 ml. of chloride solution (10 to 20% excess of silver nitrate); immediate hand shaking for 10 seconds; addition agents tested in concentrations of 0.005, 0.001, 0.0005, and 0.0001M.

These standard conditions were established through preliminary trials. Several concentrations of sodium chloride ranging from 0.005 to 0.05M all functioned alike with regard to flocculation and settling rate as well as to particle size. The silver nitrate solution is more dilute than frequently employed in published procedures, although this factor may not be critical. A pH of 6 was chosen for studying the influence of addition agents upon the flocculation rates because the precipitate normally settles very slowly at this pH; a lower pH is more desirable for practical determinations but not for testing the addition agents.

Flocculation rates were determined empirically by comparison to standard precipitates formed without addition agents; these observations were made within 3 to 5 minutes after mixing the silver and chloride solutions. Light sensitivities of the precipitates formed with addition agents were compared with those of standard precipitates formed without addition agents visually after 1-hour exposure 20 cm. from a 15-watt fluorescent lamp. Both light and electron microscope observations were made of the precipitates as quickly as possible after precipitation, so that morphology of the particles could be observed before extensive coagulation masked the individual crystals; conventional techniques were employed.

The results may be summarized as follows:

1. Electron microscope observations indicated that none of the addition agents exerted any influence upon the size of individual crystals of silver chloride.
2. Many of the addition agents increased the rate of flocculation markedly. The following agents improved the flocculation rate when present in concentrations of 0.005, 0.001, 0.0005, and 0.0001M: citric acid, tartaric acid, oxalic acid, saccharin, and naphthol yellow. The following agents improved the flocculation rate when present in concentrations of 0.005, 0.001, and 0.0005M but not when 0.0001M: benzenedisulfonic acid, potassium permanganate, potassium sulfate, and naphthol sodium disulfonate. The following did likewise when present in concentration of 0.005M but not when only 0.001M: benzyl isothiourea, naphthalenesulfonic acid, ferric chloride, picric acid, potassium dichromate, potassium bromate, and cresol; all others exhibited no influence upon the rate of flocculation.
3. Some addition agents, such as cresol, Versene, and 2-naphthol, hastened the photolytic decomposition of precipitated silver chloride; one, naphthol yellow, afforded considerable protection from light decomposition; excellent protection during 5 hours' exposure to strong reflected northern light was found when present in 0.0005M concentration, and lesser protection when only 0.0001M.

Quantitative determinations of chloride as silver chloride were made with addition agents present. The general conditions of each precipitation were similar to those listed for the small scale survey precipitations above, except that the volumes of solutions were increased so that the calculated weight of silver chloride would be within the range of 0.3300 to 0.3500 gram each time and the pH of the chloride solution was 1. The results revealed that the addition agents exert no influence upon the accuracy of the determinations.

The main reactants were mixed rapidly and, with addition agents present which enhanced flocculation rates, complete settling occurred during a 2-minute hand stirring. More important, the precipitate was bulky and loose, and so was easy to wash and to handle. No peptization occurred during washing as long as the wash liquid was about 0.1M in nitrate ion. Naphthol yellow is especially interesting because it protects the precipitate from photolytic decomposition up to the final washing and because the disappearance of the yellow color from the precipitate serves as an indicator to show when the washing is complete.

Nickel Dimethylglyoxime Precipitations. A conventional procedure was used in the nickel dimethylglyoxime precipitations to test the effects of addition agents. Approximately 300 precipitations were conducted. None of the addition agents listed in Table I exerted any noticeable influence upon the characteristics of the precipitate of nickel dimethylglyoxime.

SUMMARY

In the precipitation of barium sulfate, several addition agents were found to influence the crystal morphology, especially its size, and none was found to influence the extent of coprecipitation, either beneficially or adversely. In the precipitation of silver chloride, several addition agents influence the flocculation rate, none influences the individual particle size, and one (naphthol yellow) provides protection from photolytic decomposition. In the precipitation of nickel dimethylglyoxime, none of the addition agents tested exerts any influence upon the characteristics of the precipitated crystals.

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Determination of Sodium Monoxide in Sodium

An Addendum

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THE interest in liquid metal coolants and in other applications of the mercury extraction method as in the determination of oxygen in zinc (*2*) and in tin (*5*) has increased rapidly. In the paper by Pepkowitz and Judd on the determination of sodium monoxide in sodium (*3*), the data given indicate a precision within ±0.005% on replicates from a given sample. However, the over-all precision on a series of samples was within 0.01%.

During the 3 years since the publication of the original paper, minor modifications in the procedure have resulted in a significant increase in the precision obtained by the mercury extraction method (*4*).

Table I. Precision Data for Determination of Oxygen in Sodium

Sample No.	Oxygen, % Sample A	Sample B	Difference
Distilled sodium	0.007	0.007	0.0
Heat exchanger	0.015	0.013	0.002
6-82	0.006	0.007	0.001
6-87	0.003	0.005	0.002
P-22	0.018	0.011	0.007
BDE-5	0.008	0.005	0.003
A-24	0.006	0.005	0.001
6-89	0.004	0.003	0.001
BDE-6	0.008	0.007	0.001
6-90	0.010	0.009	0.001
6-91	0.005	0.005	0
6PH-1	0.012	0.012	0
6-26	0.008	0.009	0.001
6-95	0.008	0.005	0.003
BCT-1	0.012	0.011	0.001
6-98	0.034	0.031	0.008
		Mean	0.0017
		Standard deviation	±0.0017

The inherent precision was also demonstrated by the adaptation to a remotely operated sampling and analytical system (*1*) in which a precision within 0.001% was reported. In the course of the routine application of the method over the past few years, a number of different analysts have used the method with a somewhat uniform precision as shown in Table I.

These data are given in pairs. Each pair is the single value obtained on duplicate sodium samples and not on portions of the same sample. The standard deviation for precision of the differences between duplicate pairs is ±0.0017, which is a significant increase in precision over the data originally reported.

Two modifications in the method were made which allow for this increase in precision. The first is an increase in the purity of the blanket gas with respect to oxygen. This was accomplished by passing the gas through NaK bubblers (*1*) to remove the oxygen instead of over hot copper. The NaK bubbler is much more convenient as well as effective and the present system has been in continuous use for ~2.5 years without any maintenance.

The second modification is to heat the extractor by brushing with a gas flame during the amalgamation step. In the original procedure the extractor was cooled with an air blast in order to prevent undue strains on the glass reactor. However, experience has shown that no adverse effects are caused by the elevated temperature but rather the amalgamation is more complete at the elevated temperature.

The technique has been applied to sodium-potassium alloy (NaK) and to lithium.

The NaK sample is easily handled by freezing the NaK contained in the glass sampling tube on dry ice. It will remain frozen during the initial steps of the procedure, so that it can be handled in the same manner as a solid sodium sample. The apparatus is modified slightly in that the end of the rubber sleeve which holds sample A in Figure 1 of the original paper (*3*) is closed with a length of glass tubing sealed at the end. This is immersed in a dry ice slurry during the remainder of the analysis to keep the residual NaK sample frozen. By this simple means the original procedure can be adhered to, even though NaK is liquid at room temperature and much more reactive than sodium metal.

Somewhat more elaborate precautions are required for lithium, and the description of this apparatus will be the subject of a forthcoming communication.

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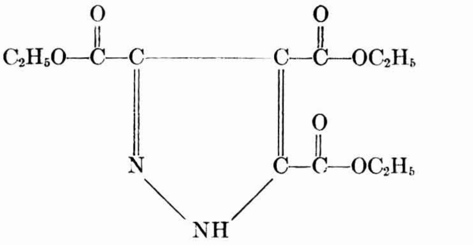
77. 3,4,5-Tricarbethoxypyrazole

Contributed by JONATHAN PARSONS, Henry Ford Hospital, Detroit, Mich., and
WALTER C. McCRONE, Armour Research Foundation of Illinois Institute of Technology, Chicago 16, Ill.



Structural Formula for 3,4,5-Tricarbethoxypyrazole

3,4,5-TRICARBETHOXYPYRAZOLE is very soluble in most organic solvents—e.g., ethyl alcohol, benzene, and amyl acetate—and is slightly soluble in water, carbon tetrachloride, and acetone. It can be recrystallized from benzyl alcohol on a microscope slide (Figure 1). Large well-formed crystals can be obtained from benzyl alcohol solution by touching a drop containing the good crystals with a corner of filter paper to remove excess solution and then teasing the best crystals away from the drop with a needle. Sliding the crystals with the needle across the slide wipes away the excess solution and precludes recrystallization of small crystals on the well-formed crystals.

CRYSTAL MORPHOLOGY

Crystal System. Monoclinic.

Form and Habit. Rods and tablets elongated parallel to *b* showing the orthopinacoid, {100}; orthodome, {101}; and clinodome, {011}.

Axial Ratio. $a:b:c = 1.417:1:1.310.$

Interfacial Angles (Polar). $101 \wedge 10\bar{1} = 94°32'$. $011 \wedge 0\bar{1}1 = 104°48'$. $101 \wedge \bar{1}00 = 136°48'$.

Beta Angle. 97° 35′.

X-RAY DIFFRACTION DATA

Space Group. $P2_1 - C_2^2$.

Cell Dimensions. $a = 10.38$ A.; $b = 7.33$ A.; $c = 9.60$ A.

Formula Weights per Cell. 2 (1.996 calculated from x-ray data).

Formula Weight. 284.14.

Density. 1.300 (displacement); 1.304 (x-ray).

Principal Lines

d	I/I_1	*d*	I/I_1	*d*	I/I_1	*d*	I/I_1	*d*	I/I_1
10.28	2	4.51	1	3.20	1	2.41	1	1.99	2
8.12	1	4.21	5	3.10	5	2.36	5	1.92	3
7.50	10	4.08	1	2.98	3	2.29	1	1.88	1
6.53	6	3.97	7	2.89	4	2.25	1	1.85	2
5.96	3	3.84	9	2.84	4	2.20	1	1.80	3
5.71	2	3.66	6	2.73	2	2.17	2	1.70	1
5.20	7	3.58	7	2.65	3	2.13	1	1.65	2
4.87	3	3.44	5	2.60	1	2.09	4	1.58	1
4.73	5	3.31	5	2.47	3	2.05	3	1.49	2

OPTICAL PROPERTIES

Refractive Indices (5892 A.; 25° C.). $\alpha = 1.485 \pm 0.003$. $\beta = 1.556 \pm 0.002$. $\gamma = 1.582 \pm 0.002$.

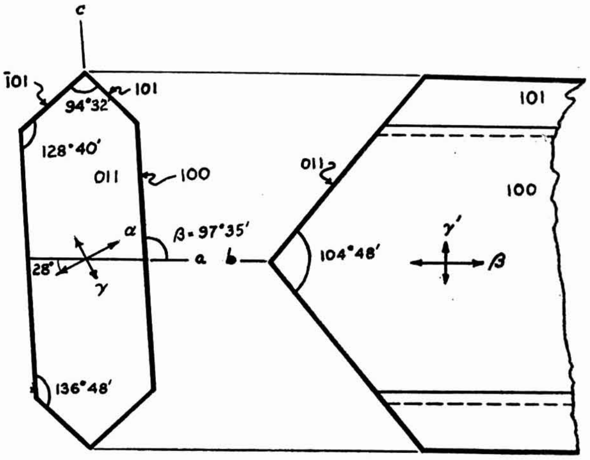


Figure 3. Orthographic Projection of Typical Crystals of 3,4,5-Tricarbethoxypyrazole

Optic Axial Angles (5893 A.; 25° C.). $2V = (-)60°$ (calculated from α, β, and γ). $2E = 103°$.

Dispersion. $r > v$, strong.

Optical Axial Plane. 010.

Acute Bisectrix. $\alpha \wedge a = 28°$ in obtuse β.

Molecular Refraction (*R*) (5893 A.; 25° C.). $\sqrt[3]{\alpha\beta\gamma} = 1.540$. *R* (calcd.) = 66.7; *R* (obsd.) = 68.6.

FUSION DATA. 3,4,5-Tricarbethoxypyrazole melts without sublimation or decomposition at 92–93° C. The melt supercools to a viscous liquid and remains liquid indefinitely. On rewarming, crystallization may occur; however, even seeding at 80° to 85° C. results only in slow growth of rods (Figure 2) with a variety of profile angles. All refractive indices observed are higher than that of the melt. Some crystals show an optic axis interference figure [$2V = (-)60°$; $r > v$, strong].

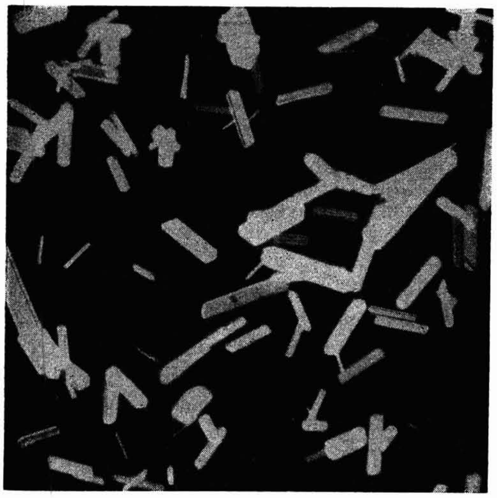


Figure 1. Typical Crystals of 3,4,5-Tricarbethoxypyrazole from Benzyl Alcohol on Microscope Slide

Crossed Nicols

Figure 2. Crystals from Melt

Crossed Nicols

CONTRIBUTIONS of crystallographic data for this section should be sent to Walter C. McCrone, Analytical Section, Armour Research Foundation of Illinois Institute of Technology, Chicago 16, Ill.

AIDS FOR THE ANALYST

Multiple-Color Development Method for Use in Paper Chromatography.

Charles C. Woodward and Glenn S. Rabideau, The Plant Research Institute, The University of Texas, and Clayton Foundation for Research, Austin, Tex.

PARTITION chromatography with filter paper is being employed widely for the tentative identification of organic compounds of plant or animal origin. In order to identify several different types of metabolic products using a single chromatogram, a method is here reported by which amino acids, organic acids, and sugars can be detected using, sequentially, three color-developing indicators. Further treatment affords differentiation between reducing and nonreducing sugars.

A two-dimensional chromatogram was made using a sample of the alcohol extract of plant or animal material. The following solvents were used: (1) 3 grams of phenol, 1 ml. of water, and a volume of 90% formic acid equivalent to 1 volume % of the phenol-water mixture; and (2) 1 ml. of isopropyl alcohol, 1 ml. of *tert*-butyl alcohol, 3 ml. of benzyl alcohol, 1 ml. of water, and a volume of 90% formic acid equivalent to 1 volume % of the water-alcohol mixture.

The chromatograms were dried after solvent development, sprayed with a 0.2% ninhydrin [Dent, C. E., *Biochem. J.*, **43**, 169 (1948)] solution in water-saturated 1-butanol, and dried at 70° C. in an oven. Spots denoting amino acid locations were then marked with a soft lead pencil, their identities established, and concentrations evaluated by visual comparison with chromatograms prepared by using standard samples of pure amino acids.

Organic acid identifications were made by spraying the same chromatogram with 0.1 weight-volume % solution of methyl red in alcohol. This solution was adjusted with sodium hydroxide to a pH where the solution just turned orange on the paper. Methyl orange was also used as an organic acid indicator, but has the disadvantage of giving less intense spots than does methyl red. The chromatogram was allowed to dry in air and spots denoting organic acids were marked and evaluated for identity and concentration by comparison with spots produced by standard samples of pure organic acids similarly treated.

Following acid detection, 3,5-dinitrosalicylate reagent was sprayed on the paper for the identification of sugars [Jeanes, Allene, Wise, C. S., and Dimler, R. S., ANAL. CHEM., **23**, 415 (1951)]. The chromatogram was air-dried and placed in an oven at 105° until the dark brown spots, denoting reducing sugars, reached maximum intensity. The chromatogram was then stored in darkness at room temperature for 2 weeks, during which time the nonreducing sugars appeared as gray-green colored spots. The original reducing sugar spots remained brown. Both at the beginning and at the end of this storage period the kinds and concentrations of sugars present were interpreted by comparison with spots produced by standard samples of pure sugars similarly treated.

Relative sensitivity of the color-developing spray reagents afforded accurate identification with the following minimum concentrations: amino acids, 1 to 5γ, organic acids, about 25γ, reducing sugars about 15γ, and nonreducing sugars 60γ, per chromatogram. Although these relative sensitivities are somewhat below figures quoted elsewhere, some sensitivity was sacrificed in favor of the advantage of the multiple detection of substances on a single paper chromatogram.

A better interpretation of organic acids present in low concentrations could be made, if, in addition to the regular two-dimensional chromatogram, a duplicate sample in one corner of the chromatographic paper was used for a one-dimensional chromatogram. When the first development was complete and the paper air-dried, the one-dimensional chromatogram strip was cut off and sprayed for organic acids with 0.1 weight-volume % solution of bromocresol green or methyl red in alcohol. This afforded a better evaluation of the organic acids present in low concentration because of less diffusion of the spots.

Many attempts were made to improve the degree of separation of these compounds on the chromatogram. Present results indicate, however, that where spots of substances of different types of compounds—e.g., sugars, organic acids, or amino acids—overlap, they do not interfere with the determination of compounds in the other groups because, as each of these groups is determined sequentially, the previously indicated spots fade.

Polyethylene-Coated Glass Flasks.

George A. Simmons, Jr., Department of Chemistry, Birmingham-Southern College, Birmingham 4, Ala.

THE author was recently confronted with the problem of vacuum-evaporating a strongly caustic solution without introducing silica. Obviously, a glass flask could not be used for the still pot. Polyethylene plastic bottles, although chemically inert and reasonable in cost, are so flexible that they collapse under pressure. A polyethylene-coated glass flask would combine the strength of glass and the inertness of the plastic. The common techniques of coating by painting, spraying, or dipping could not be used, because polyethylene is resistant to practically all solvents and does not melt to a free-flowing liquid. The plastic would adhere when brought in contact with hot glass, but coats formed by this simple process tended to separate from the glass when the temperature varied and could not be replaced. The following procedure gives a uniform and complete coat which does not loosen with temperature fluctuations.

The plastic is obtained as a granular molding powder (Du Pont's Alathon 1-P 1000 uncompounded polyethylene resin). These granules are placed, with about 1 part of ice water to 2 parts of plastic by volume, in a Waring-type blender in sufficient quantity to cover the mixing blades. The plastic is shredded to a fine powder, which, with the proper proportion of water to plastic, will creep up the glass walls of the blender. If too much water is present, the powdered plastic does not separate well from the granules; and if too little is present, the plastic forms a gummy mass. This finely powdered plastic is periodically scraped from the walls of the blender and air-dried.

The glass flask is heated to about 150° C. and then rotated while the powdered plastic (about 100 ml. for a 1-liter flask) is poured into it so that the plastic comes in contact with the area to be covered. A layer of plastic adheres at once, and the excess is poured out. The flask is heated in an oven to about 250° C. until the molten plastic begins to smoke and discolor. Slight air pressure is applied to flatten the globules of molten plastic into a smooth coat. A rubber stopper larger than the mouth of the flask can be used for applying the pressure. A glass tube through the stopper is connected to a compressed air line and pressure is applied with the hand by holding the stopper against the mouth of the flask, which is wrapped with a cloth. The flask is heated to about 150° C. to remelt the cooled plastic and more powdered plastic is added as before, forming a second layer. This layer is melted at 150° C. and again smoothed with pressure. This results in a coat of plastic which is 1 to 2 mm. thick. If a thicker coating is desired, more layers of plastic may be added in the same manner.

The success of this procedure is due to the heating of the first plastic layer to 250° C., creating a very strong bond between the glass and plastic. It is not advisable to heat subsequent layers to this temperature, especially the final layer, as the slight decomposition which occurs may destroy some of the chemical inertness of the plastic. A 2-liter round-bottomed flask coated by this method to a thickness of 1 to 2 mm. has been used repeatedly at temperatures from −20° to 50° C. with no signs of chemical attack or separation of the plastic. Such coated flasks are also shatterproof and show a definitely increased resistance to breakage.

Automatic Servo-Operated Filter Photometer.

James M. Snodgrass, Dayton E. Carritt[1], and Warren S. Wooster, Scripps Institution of Oceanography, La Jolla, Calif.

Among the most important inorganic constituents of sea water are the dissolved plant nutrients, in particular phosphate, nitrate, and silicate. All of these are commonly determined by absorptiometric methods. During recent years attempts have been made to adapt these methods for use with photoelectric colorimeters. This development has been slow and rather unsatisfactory because of the sensitivity of most such instruments to the motion of the ship.

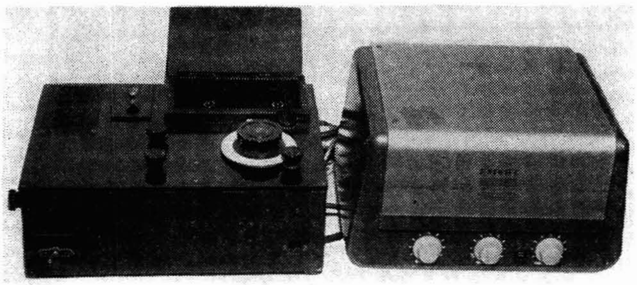


Figure 1. Filter Photometer with Amplifier

The following criteria must be met by a seagoing colorimeter, in addition to the usual requirements of accuracy and precision.

Stability. Operation must be unaffected by the motion of the ship. Because shipboard power supply is often unstable, either the instrument must be unaffected by fluctuations of voltage and frequency, or external provision must be made to minimize such fluctuations.

Reliability. Despite exposure to sea air, violent motion, and rough treatment, the instrument must give trouble-free operation during continuous use for long periods of time. It must give accurate and reproducible results in the hands of semiskilled personnel working under adverse conditions.

Versatility. A variety of analyses may be made, involving different wave lengths of light and different absorption paths. The instrument must be capable of utilizing absorption cells from 1 to 10 cm. in length.

Portability. Seagoing instruments may be taken on and off ship under adverse conditions and are frequently used on small craft.

A survey of commercial photometers revealed only one instrument which met these criteria. The Beckman Model DU spectrophotometer has been used at sea by this laboratory since 1948 and has proved satisfactory for shipboard analysis. The spectrophotometer, however, is slightly affected by the motion of the ship, is perhaps unnecessarily versatile for this work, is rather expensive, and is heavy and unwieldy to carry.

Several photometers for use in marine chemical work have recently been designed. Harvey [*J. Marine Biol. Assoc. United Kingdom*, **27**, 337 (1948)] reported an absorption meter using balanced selenium photocells, the null point being determined with a galvanometer. However, he does not mention using this instrument at sea. Ford [Anal. Chem., **22**, 1431 (1950)] describes a seagoing photoelectric colorimeter in use at the Woods Hole Oceanographic Institution and elsewhere. This instrument uses two photocells, the light to the balancing photocell being controlled by a logarithmic aperture and the balance point indicated by an electric eye tube.

The automatic servo-operated filter photometer was designed to meet the need for a rugged, relatively inexpensive seagoing instrument characterized by a high degree of precision, great flexibility, and ease of operation. It operates on the double-photocell principle, a servomotor driving the main slide wire and automatically eliminating unbalance between the signals from the two photocells. The instrument has been used during the past 3 years by the Scripps Institution of Oceanography, the Chesapeake Bay Institute, and the Pacific Oceanic Fishery Investigations of the U. S. Fish and Wildlife Service, and has proved satisfactory for shipboard use.

DESCRIPTION OF INSTRUMENT

An existing commercial photometer, the Lumetron Model 402-E colorimeter (Photovolt Corp.), was modified for automatic balancing. The electrical unbalance or error voltage between the two photocells is inverted to 60-cycle alternating current by means of a Stevens-Arnold Type 247 chopper and Triad G-10 transformer. The low level alternating current from the chopper is amplified by means of a resonant amplifier (modified Knight 93-360) to a suitable level for the direct operation of a low-power servomotor (Bodine Type KCI-22, 17 r.p.m.). The servomotor drives the main slide-wire in the proper direction to reduce the photocell error voltage to zero. At this point the linear dial at-

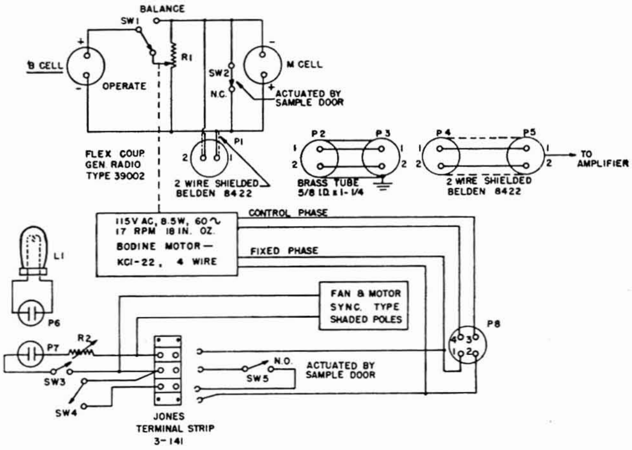


Figure 2. Measuring Circuit

L_1. Radiant projection, 100 watts, 120 volts
P_1, P_4, P_5. Amphenol 80-MC2M
P_2, P_3. Amphenol 80-PC24
P_6. Jones plug, P-302-CCT
P_7. Jones receptacle S-302-A8
P_8. Amphenol 77-MCP-4
R_1. 500-ohm pot. Helipot SG71
R_2. 75-ohm, 1.15-ampere max., ohmite 0450, Model K, 100 watts
SW_1. SPDT toggle
SW_2, SW_5. Microswitch
SW_3, SW_4. SPST toggle

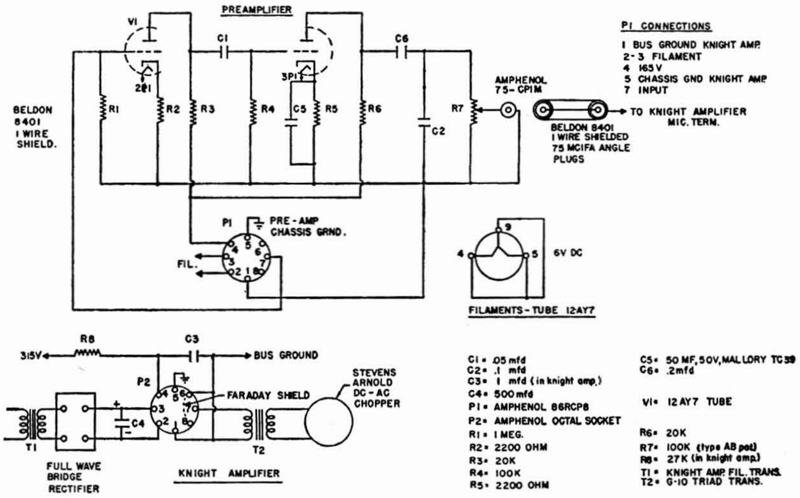


Figure 3. Preamplifier Circuit

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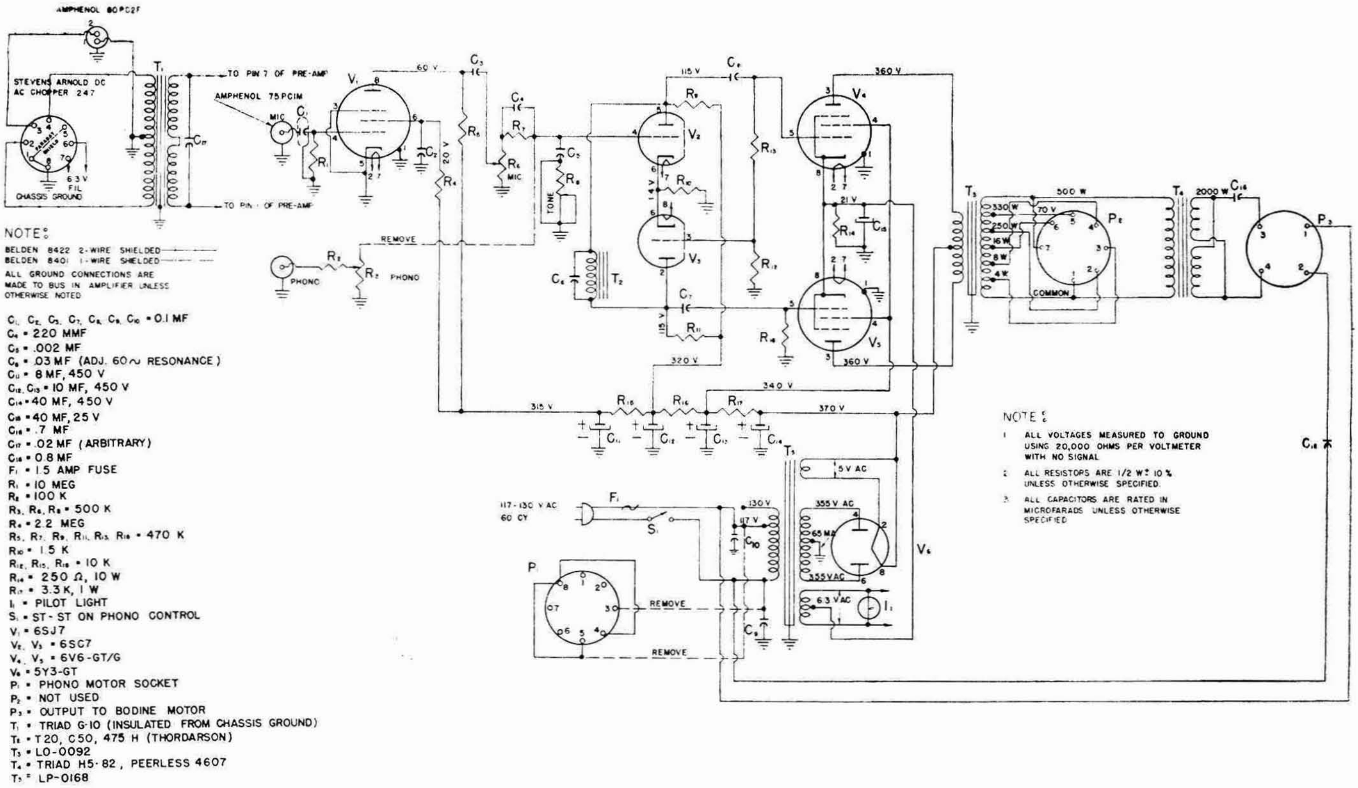
[1] Present address, Chesapeake Bay Institute, The Johns Hopkins University, Annapolis, Md.



NOTE:

BELDEN 8422 2-WIRE SHIELDED
BELDEN 8401 1-WIRE SHIELDED

ALL GROUND CONNECTIONS ARE MADE TO BUS IN AMPLIFIER UNLESS OTHERWISE NOTED

C_1, C_2, C_3, C_7, C_8, C_9, C_{10} = 0.1 MF
C_4 = 220 MMF
C_5 = .002 MF
C_6 = .03 MF (ADJ. 60~ RESONANCE)
C_{11} = 8 MF, 450 V
C_{12}, C_{13} = 10 MF, 450 V
C_{14} = 40 MF, 450 V
C_{15} = 40 MF, 25 V
C_{16} = .7 MF
C_{17} = .02 MF (ARBITRARY)
C_{18} = 0.8 MF
F_1 = 1.5 AMP FUSE
R_1 = 10 MEG
R_2 = 100 K
R_3, R_6, R_8 = 500 K
R_4 = 2.2 MEG
R_5, R_7, R_9, R_{11}, R_{13}, R_{18} = 470 K
R_{10} = 1.5 K
R_{12}, R_{15}, R_{16} = 10 K
R_{14} = 250 Ω, 10 W
R_{17} = 3.3 K, 1 W
I_1 = PILOT LIGHT
S_1 = ST-ST ON PHONO CONTROL
V_1 = 6SJ7
V_2, V_3 = 6SC7
V_4, V_5 = 6V6-GT/G
V_6 = 5Y3-GT
P_1 = PHONO MOTOR SOCKET
P_2 = NOT USED
P_3 = OUTPUT TO BODINE MOTOR
T_1 = TRIAD G-10 (INSULATED FROM CHASSIS GROUND)
T_2 = T20, C50, 475 H (THORDARSON)
T_3 = LO-0092
T_4 = TRIAD H5-82, PEERLESS 4607
T_5 = LP-0168

NOTE:

1. ALL VOLTAGES MEASURED TO GROUND USING 20,000 OHMS PER VOLTMETER WITH NO SIGNAL
2. ALL RESISTORS ARE 1/2 W ± 10% UNLESS OTHERWISE SPECIFIED.
3. ALL CAPACITORS ARE RATED IN MICROFARADS UNLESS OTHERWISE SPECIFIED

Figure 4. Servoamplifier Circuit

tached to the slide wire reads percentage transmittancy directly (by means of a logarithmic dial, absorbancy can be read directly) (Figures 1 to 4).

Essentially monochromatic light is obtained by use of interference-type filters peaked at the desired wave length. Response characteristics of the instrument are controlled by the spectral response of the photocells and by the amount of energy passed by the filter. It is possible to adjust the sensitivity by varying the intensity of the light source and by adjusting the amplifier gain. A preamplifier was added to the circuit, so that high sensitivity is available under most working conditions.

In order to prolong the life of the light source and to prevent fatigue of the photocells, two microswitches are operated by the lid to the absorption cell compartment. When the lid is opened, one switch turns off the light and the other shorts together the two photocells.

During the design of the filter photometer, the following details were found to be of importance.

It is very important to use a working slide wire having very low noise characteristics (less than 5μv.). For this purpose the Helipot SG-71 500-ohm potentiometer was found satisfactory.

The instrument is sensitive to voltage fluctuations of ±2% or greater. For shipboard installations, Sorensen voltage regulators have been satisfactory.

If the amplifier and photometer are to be used at sea, it is important to install about 20 watts of heater resistors, which should be continuously energized. The heater resistors should be large enough to operate at a low surface temperature (such as a 50-watt resistor actually dissipating 10 watts).

Erratic sensitivity in early instruments was found to be due to inadequate bearings in the Bodine servomotor. When these bearings were replaced with precision bearings, this trouble was eliminated.

METHOD OF OPERATION

Although the filter photometer may be balanced for 100% transmittance against a cell filled with solvent, customarily it is balanced against an air path. Absorbancy of the cell itself is determined by appropriate cell checks and reagent blank determinations. This obviates the need for matched cells and reduces the number of cells required. Handling of absorption cells, and hence breakage at sea, is also reduced.

In making measurements, the instrument is first balanced for 100% transmittance, by closing the cell compartment lid and throwing switch SW_1 to the balance position, thus using the full resistance of the slide wire. The balancing photocell is then rotated manually until electrical unbalance is eliminated. At this point the motor, and hence the dial attached to the slide wire, stops rotation. The cell containing the sample is then placed in the cell compartment, switch SW_1 is thrown to the measuring position, and the compartment lid is closed. The slide-wire dial then rotates until balance is effected. Percentage transmittancy is read directly from the dial.

If the power source is sufficiently stable, the initial balancing need only occasionally be carried out. Adjustments of light source intensity and amplifier gain affect the balance point and should be made prior to initial balancing.

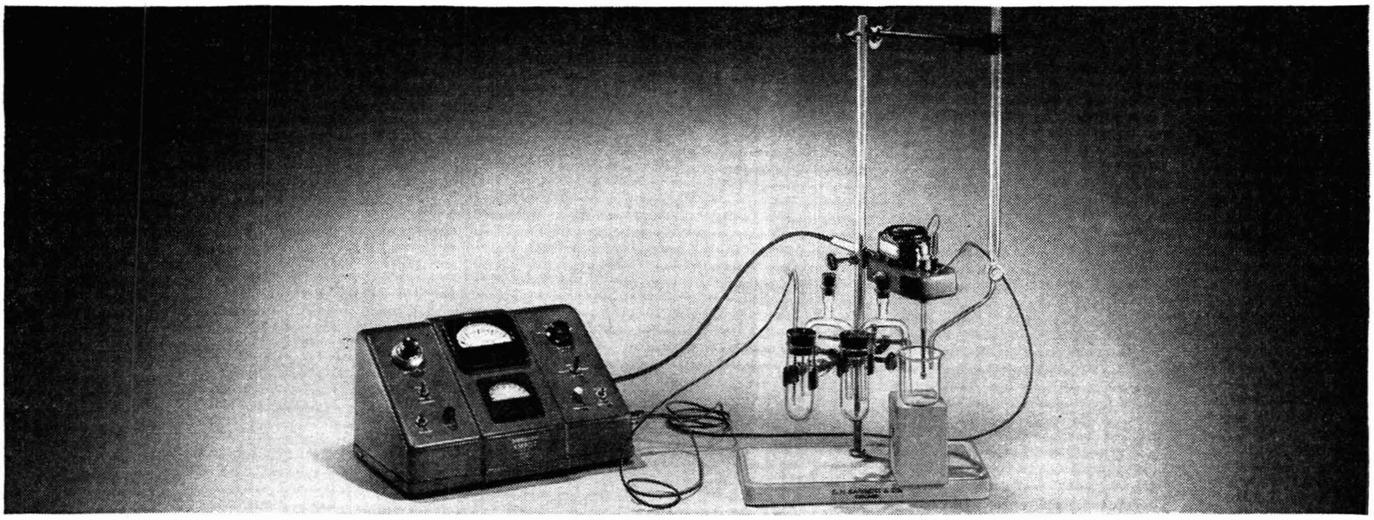
PRECISION OF MEASUREMENTS

In order to establish the precision of measurement of percentage transmittancy of the automatic servo-operated filter photometer, a series of measurements was made of the transmittancy of a light shade AKLO filter (Color Spec. No. 1-58, Corning Glass Works). This filter has a fairly flat response in the vicinity of 700 mμ, its approximate spectral transmittance at 700 mμ being 0.35. A Baird Associates interference filter peaked at 696 mμ was used to render the incident light essentially monochromatic. A series of 78 readings gave the following results:

	Average	Std. Dev.	Range
Percentage transmittancy	46.56	0.09	46.4–46.8
Absorbancy	0.332	0.0008	0.333–0.330

CONTRIBUTION from Scripps Institution of Oceanography, New Series, No. 630. This work was supported by the Marine Research Committee, Department of Natural Resources, State of California.

Amperometric Titrations



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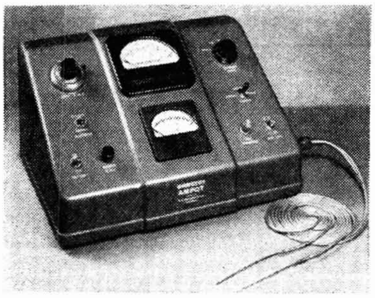

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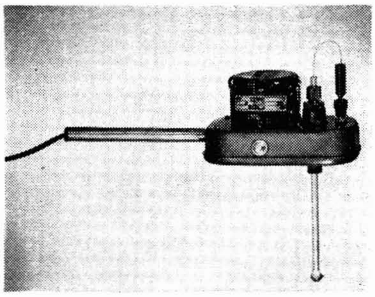

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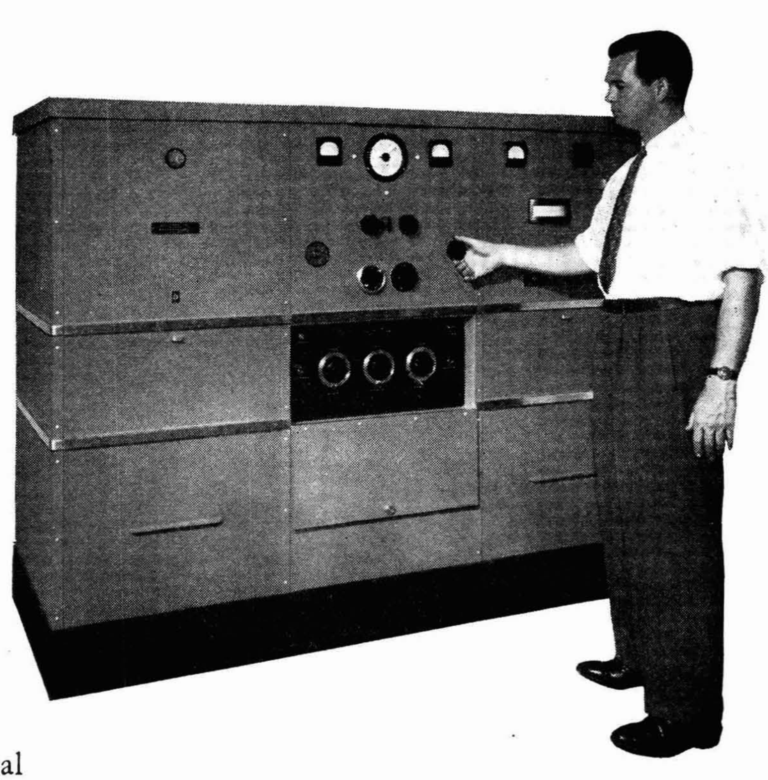

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Scientific Apparatus Makers Look at Tariffs, Sales Prospects, Taxes, and Research

BOCA RATON, FLA.—The unsung hero of the scientific instrument industry came into his own last month at the four-day meeting of the laboratory and optical sections of the Scientific Apparatus Makers Association.

C. P. Tebeau, professor of chemistry at the University of Miami, summarized his views about the unsung hero in these words:

> The sales representative has made himself an indispensable part of scientific research; the work of the salesman has been such as to call for general commendation.... Certainly the scientist who discusses his needs with the representatives who call on him will receive invaluable suggestions and courteous help. How the company can afford to provide us with these very helpful people is, fortunately, their headache—not ours. All we know is that we are glad that they find some way to do it.

Dr. Tebeau's address was part of a panel discussion, "The Scientific Sales Representative—His Selection, Training and Contribution to Science." The sum and substance of the discussion was that (1) salesmen—the right kind—are hard to find; and (2) still better training is highly desirable.

SAMA Tariff Position

One entire morning session of the SAMA conference was given over to a discussion of the tariff. In an official statement made by the officers of SAMA, the opinion was expressed that there now exists neither policy, procedure, nor agency through which an industrial operation indispensable to national security can be so defined and safeguarded.

The SAMA statement suggests that the Commission on Foreign Economic Policy (the Randall Committee) recommend to the President and Congress:

1. That there be created an independent commission of seven members consisting of the Secretary of Defense, the Secretary of Commerce, the Secretary of Labor, the Secretary of State, the Secretary of the Treasury, the Director of Defense Mobilization, or their qualified designees, and a chairman appointed by the President with power to control imports, through the issue of licenses or otherwise, of any materials, products, or articles similar to those produced by each of such indispensable industries for the purpose of creating or maintaining sound, adequate, and efficient domestic industries necessary to our national defense.

2. That there be created by this commission an extraordinary classification of industrial operations to be so safeguarded as indispensable to national defense to the end that minimum levels of operational defense can be established or maintained without undue curtailment due to imports. It is further recommended that the following industry criteria be considered in determining both the extraordinary classification and minimum levels of operations necessary to national defense:

(*a*) The necessity for trained personnel—unique skills not available in other industrial operations; the abnormal time required for training—in excess of normal industrial training periods; and the basic group necessary to train other personnel.

(*b*) The necessity for continuous research to assure leadership in scientific developments.

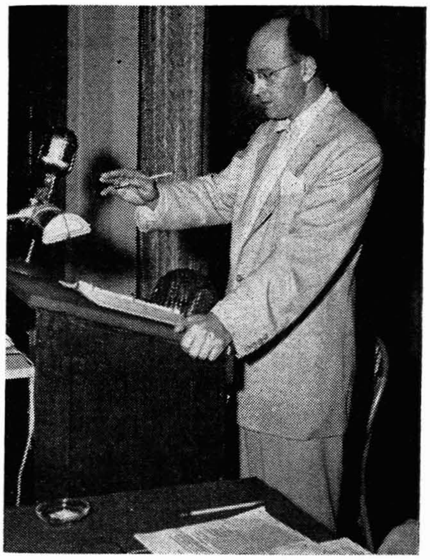
(*c*) The necessity for a constant relationship to defense needs and developments.

Sales and Use Taxes

Another highlight of the midyear meeting was an address on "Sales and Use Tax," delivered by James E. Elworth of the law firm of Pope and Ballard.

Mr. Elworth pointed out that during the depression of the thirties, many states turned to sales taxes to bolster their sagging revenues. As with any new tax, taxpayers quickly sought ways to avoid it. The tax operated successfully where residents bought from local merchants. But buyers living near a state line soon learned that they could avoid the tax by making their purchases in an adjacent state. They also discovered that if they placed orders with out-of-state sellers, the tax could be avoided. This was based on the fact that the commerce clause of the Constitution prohibited states from taxing transactions in interstate commerce.

As the states became aware of these serious limitations on their taxing power, they sought ways to plug the loophole. According to Tax Expert Elworth, the result was a tax on the use of merchandise bought outside a state's boundary. The Supreme Court of the U. S. has upheld this type of tax. Practically every state which has a sales tax now has a use tax which provides that if a resident uses or consumes property on which the sales tax has not been paid, he is liable for the use tax. The rates, according to the speaker, are always the same.



Sales and taxes were discussed by James E. Elworth of Pope and Ballard, attorneys for SAMA

In most sales and use tax states, the statutes require out-of-state sellers, under various factual situations, to collect the use tax on sales which are exempt from sales tax.

Elworth closed his report to the SAMA organization by stressing the fact that manufacturers and dealers should give very serious study to the present sales and use taxes, since practically all producers and dealers of scientific equipment and laboratory apparatus sell across state lines. Further clarification of the situation is anticipated shortly when a case recently decided by the Maryland Court of Appeals is reviewed by the U. S. Supreme Court.

Research Expenditures

In a report to the SAMA membership the officers pointed out that of the $1.6 billion spent in 1951 for research by all the companies included in the report, the scientific instrument industry's share was $91,400,000. These figures are based on a recent report issued jointly by the Bureau of Labor Statistics and the U. S. Department of Defense and includes only the volume of research done by private organizations.

Western Spectroscopy Conference at Berkeley

The first meeting of the Western Spectroscopy Conference will be held Feb. 4 and 5 at the University of California, Berkeley. Last April the Consolidated Engineering Corp., Pasadena, sponsored discussion at its plant on the formation of a regional spectroscopy group, with favorable reaction and cooperation.

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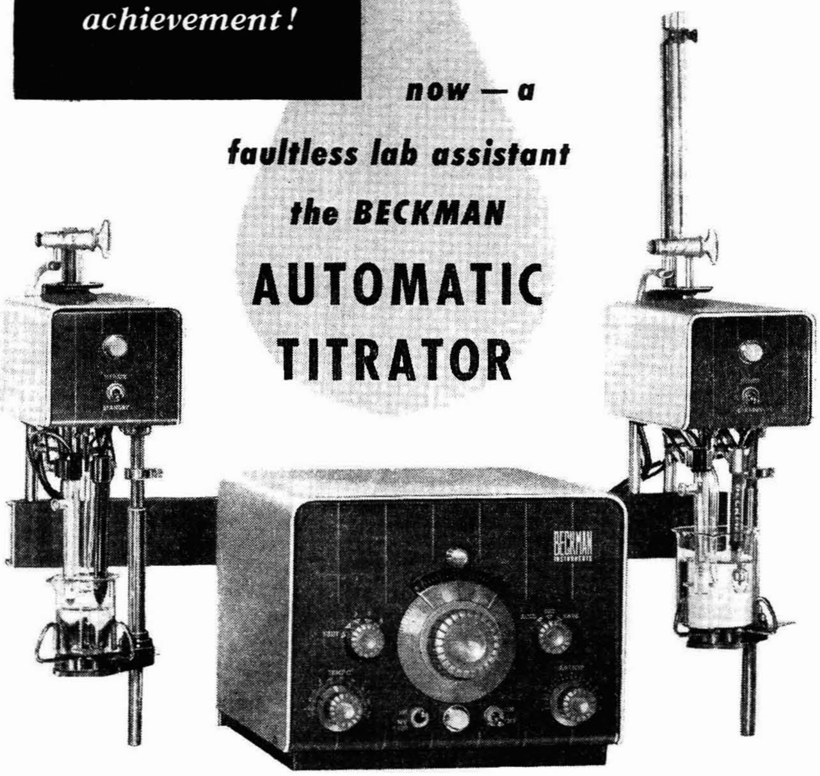


Efforts were made to make the meeting attractive to academic, industrial, and government spectroscopists. Field of coverage will embrace molecular spectroscopy. It was agreed to keep the meeting on an informal basis, with one or two invited speakers at each of four half-day sessions, each talk followed by general discussion and informal presentation of pertinent, current work by others. No publication of either invited talks or discussions is planned. Registration fee will be $5.00 to all interested and includes dinner. Fee for students is $1.00; $4.00 including dinner.

Kenneth Pitzer of the University of California will open the conference at 9:30 Thursday morning.

Lifetimes of Photoactivated Molecules. G. K. ROLLEFSON, University of California.

The Interpretation of High Molecular Weight Mass Spectra of Hydrocarbon Systems. M. J. O'NEAL, JR., Shell Oil Co.

Principles of Nuclear Induction. FELIX BLOCH, Stanford University.

Applications of Nuclear Magnetic Resonance to Chemical Systems. J. N. SHOOLERY, Varian Associates.

Infrared Spectra of Solids. J. C. DECIUS, Oregon State College.

Microwave Spectra of Molecules with Hindered Internal Rotation. R. J. MYERS, University of California.

Spectroscopy Seminar At Gainesville

The Southern Association of Spectrographers will hold its second annual Seminar on Spectroscopy and its spring meeting at the University of Florida, Gainesville, Feb. 17 to 19. The morning discussion of the first day will be on Interpretation of Spectra for Qualitative and Quantitative Analysis, Computational Methods, and Analytical Curves. The afternoon session will cover Instrumentation for Emission Spectrochemical Analysis. The morning session of Feb. 18 will take up Excitation Sources and Their Application, and Production of Spectra for Quantitative and Qualitative Analysis; the afternoon, Sampling, Sample Preparation, and Standards.

On Feb. 19 the spring meeting will include presentation of technical papers, panel discussions, and a business meeting.

Further information may be obtained from William T. Tiffin, College of Engineering, University of Florida, Gainesville, Fla.

Sensory Panel Testing

An evening course in sensory panel testing for the food and allied trades will be offered Monday evenings, beginning March 15, by New York University. Designed for laboratory, quality control, production, and administrative personnel concerned with flavor and odor differences and preferences, the course will include practical methods for solving problems involving organoleptic evaluation of products that cannot be solved by other analytical procedures. Instructor will be Jack K. Krum, research chemist, National Biscuit Co.

Registration will be at the Division of General Education, 1 Washington Square North, New York 3, N. Y., beginning January 18.

ANALYST'S CALENDAR

Fifth Annual Southeastern Symposium on Industrial Instrumentation. University of Florida, Gainesville, Fla., February 1 to 3

Instrument Society of America. Ninth Annual Regional Conference. Hotel Statler, New York, N. Y., February 4

New York Microscopical Society. Symposium on Industrial Microscopy. American Museum of Natural History, New York, N. Y., February 5 and 6

Meeting-in-Miniature, New York Section, American Chemical Society. Hunter College, New York, N. Y., February 12

Metropolitan Microchemical Society. American Museum of Natural History, New York, N. Y., February 18

American Chemical Society. 125th National Meeting, Kansas City, Mo., March 24 to April 1, 1954

Symposium on Instrumentation. University of Michigan, Ann Arbor, Mich., May 24 to 27, 1953

Seventh Annual Summer Symposium. Recent Developments in Titrimetry. University of Minnesota, Minneapolis, Minn., June 18 and 19

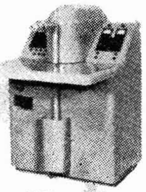
BOOK REVIEWS

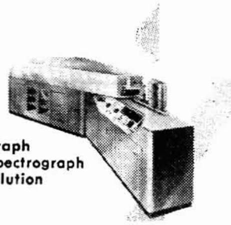
Practical Chromatography. *Robert C. Brimley* and *Frederick C. Barrett.* Introduction by *E. C. Bate-Smith.* 128 pages. Reinhold Publishing Corp., New York, N. Y., 1953. Price $5.00.

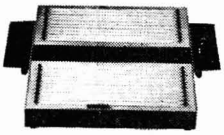
F. C. Barrett and the late R. C. Brimley have produced an excellent little monograph covering both paper and column chromatography. Their schematic presentation of the probable mode of action of separations by partition chromatography is a delight to anyone wishing to explain this now classical procedure to students. The three general types of column chromatography—partition, adsorption, and ion exchange—as well as three procedures for operating chromatographic columns—elution, frontal analysis, and displacement development—are described in the introduction.

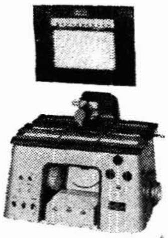
Chapter 2 gives a brief resume of the methods of paper chromatography, describing some of the original apparatus and solvents of Consden, Gordon, and Martin together with a few of the more recent modifications.

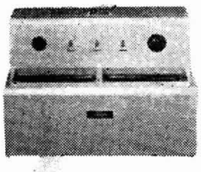
Chapter 3 describes very briefly methods for the quantitative estimation of materials separated on paper chromato-

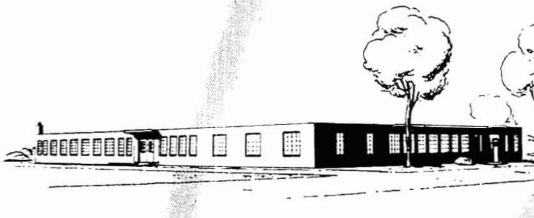


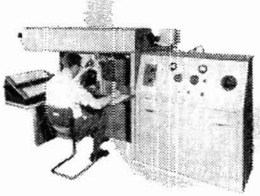












grams. These consist of three general methods: *measurement of spot area*, measurement of the total density of color over the length of the spot or more simply from its maximum color density, and excision of the spot followed by microchemical or microbiological estimation of the substance contained therein.

Chapters 4 and 5 describe some of the techniques used in adsorption and partition column chromatography. These sections give sufficient information to allow one inexperienced in the field to prepare the more widely used types of adsorbents or phase supports but tend to minimize the difficulties which are usually encountered in practice.

Chapter 6 gives many more experimental details for the use of ion exchange resins than are presented elsewhere in the book. In fact, certain sections of this chapter are essentially verbatim accounts of published literature largely of the English school.

A description of fraction collectors, desalting apparatus, etc., is given in Chapter 7, while details of many of the more valuable spraying reagents and solvents for the chromatography of sugars, organic acids, amino acids, and metals are presented in the Appendix.

The reviewer wholeheartedly recommends this excellent little book.

RICHARD J. BLOCK

Separation et Identification des Hydrocarbures dans les Essences de Pétrole. *M. A. Bestougeff.* 110 pages. Techniques et Application du Pétrole, 11, rue Magdebourg, Paris, 1952. Price, 650 francs.

This little book reviews very briefly methods for separation and identification of hydrocarbons in petroleum products of the gasoline range. It discusses composition of straight-run distillates, thermal and catalytic distillates, and alkylates and polymers; distillation (regular, azeotropic, and extractive); adsorption; chemical treatments; physical and chemical methods of identification and determination; two schemes of analysis; and examples of a separation by distillation and by adsorption. A good bibliography contains 254 references, mostly from 1940 to 1950, but with a few earlier references.

Only 79 small pages (equivalent to about 20 pages in ANALYTICAL CHEMISTRY) are devoted to discussion. Obviously, some important topics are only briefly considered and others are omitted. For example, azeotropic distillation is covered in about 200 words.

The book is competently written and will be of interest and assistance to those wishing a very brief summary of the field. The research worker will require greater detail.

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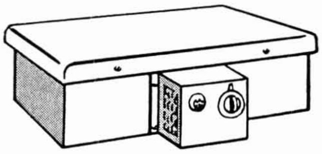

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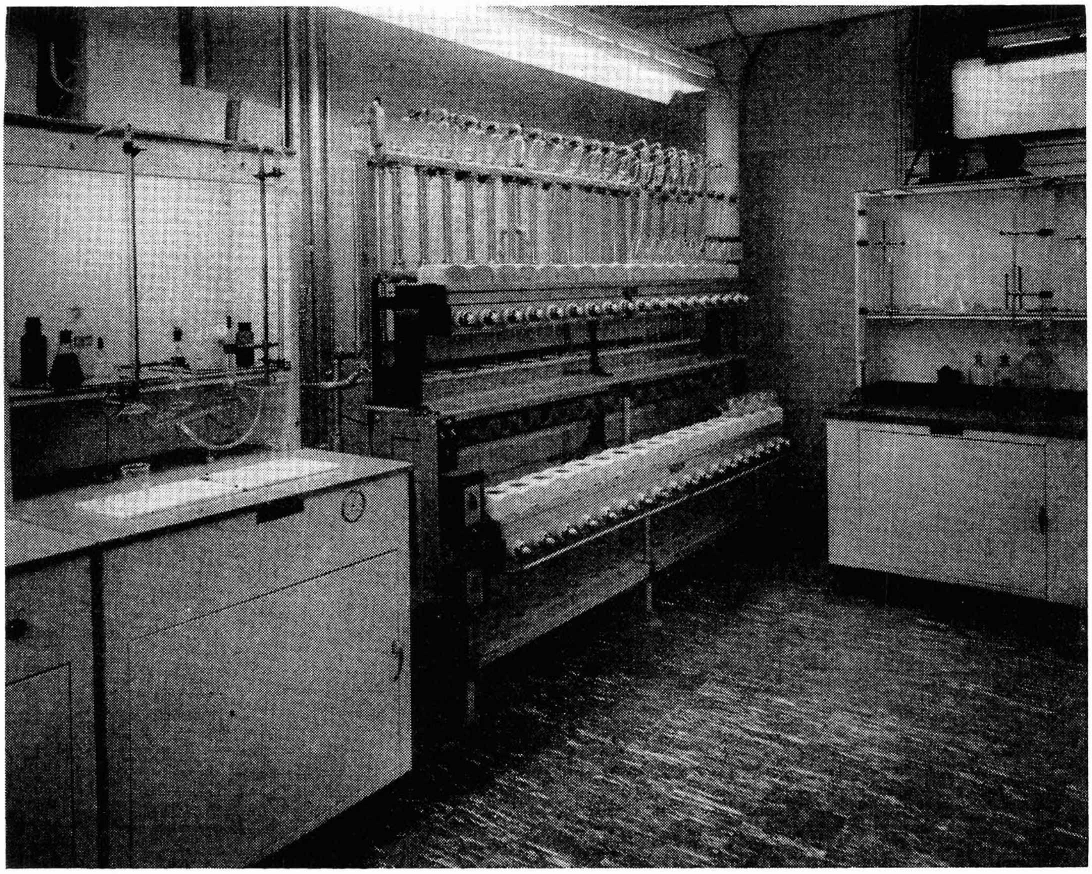
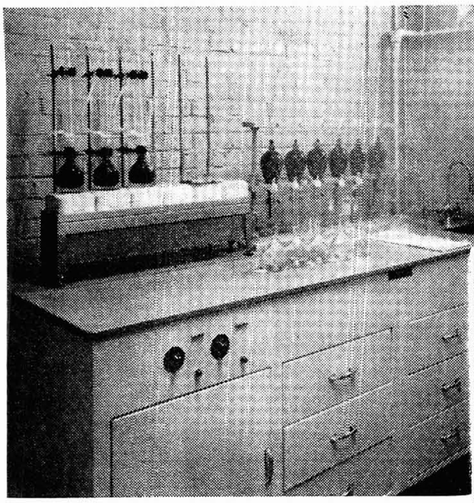


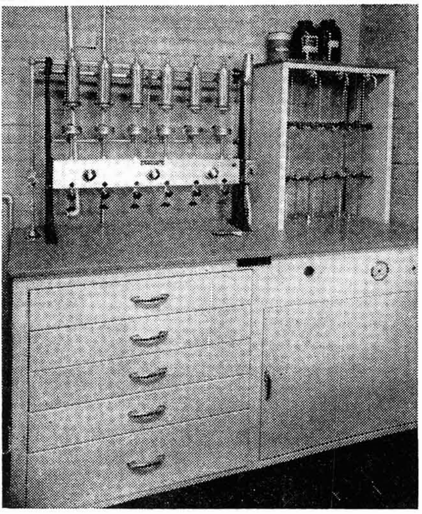
"Kjeldahl Corner" has 18 units of digestion and of distillation. Unit is all-electric with 3-heat control on heaters, thermo-water control on stills, and automatic timers on digesters. On right is lead top acid and caustic dispensing cabinet. Carboys are rolled (on low carts or sliding trays) into cabinet, and dispensing burets are filled by vacuum. Titration table on left also has solutions concealed in cabinet and utilizes pressure to fill burets

LABORATORY OF THE MONTH

- *First of a regular series to appear on these pages each month*



Variant heat table for vitamin A and other extractions and digestions requires closely controlled boiling ranges ◀



Carotene unit includes Goldfisch extractors for carotene extraction and a support rod assembly for glassware used in chromatographic procedure. A vacuum manifold furnishes vacuum to individual tables. Solvents are stored within the cupboard and solvent delivery is made by pressure or vacuum ▶

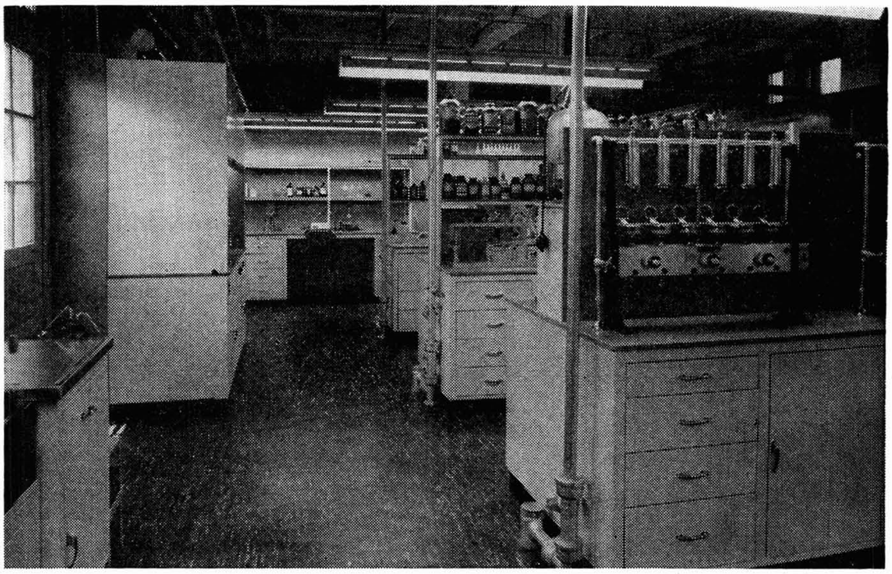
A CURRENTLY PREVALENT IDEA in the design and furnishing of laboratories is to free chemists and other scientists from housekeeping chores so that they can spend more time on work at the highest professional level. In pursuing this objective modern laboratories are being planned more efficiently and provided with the latest in apparatus and equipment.

An example of this trend is the laboratory of the Colorado Department of Agriculture at Denver. Some time ago it became apparent that the department's staff and laboratory facilities were no longer adequate to handle the growing volume of determinations in connection with control of the sales of feed, fertilizer, dairy products, and insecticides in the state. Accordingly, the department acquired a building and called in the Laboratory Construction Co., Kansas City, Mo., specialists in design, apparatus, and furniture for agricultural laboratories.

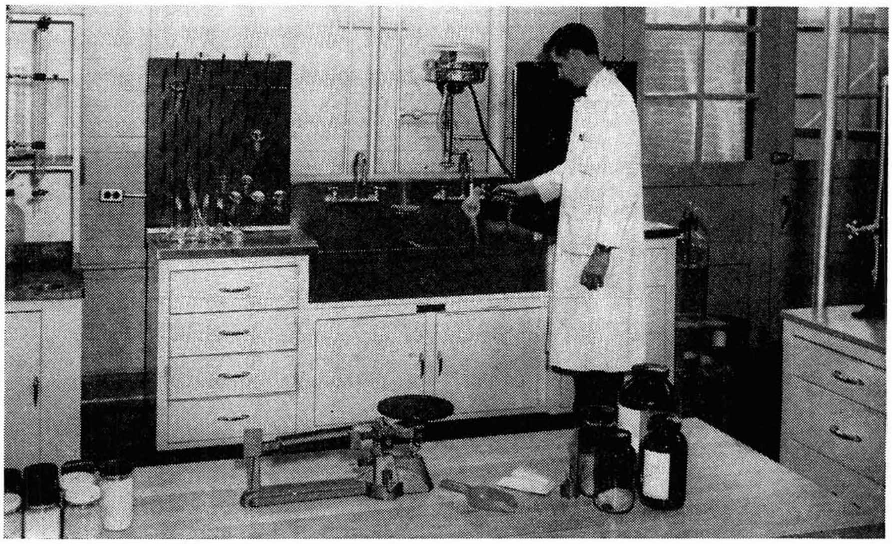
Instead of following the usual practice of installing work benches and cabinets, and then improvising the placement of apparatus and instruments, the department's staff first made a survey of the types and volume of determinations the new laboratory would have to handle. Labconco's engineers then closely integrated the furniture with the instruments and apparatus. Some equipment was custom built, but in most cases standard furniture was adapted to the specific requirements of special work areas.

As a result of careful planning and designing, the work in the new laboratory proceeds quickly, smoothly, and safely. Each operation handled in volume has its own work area. There within arm's reach are facilities for storage, dispensing, filtrations, heating, etc., and all "built in" to the cabinets. Controls, timers, and automatic features are in service wherever possible.

With the same personnel, the Colorado Department of Agriculture's laboratory can now handle a much larger volume of determinations. Chemists have been relieved of most housekeeping and common labor jobs, and are free to devote their time to the work for which they were trained.

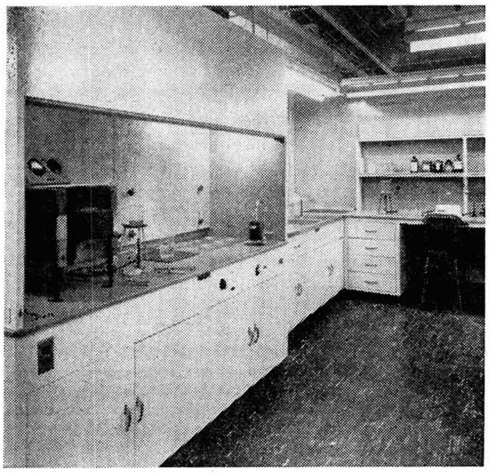


Aisle view of three center tables. Work here is varied, but note two Goldfisch fat extractors on first table. Asbestos back shield is safety feature, and drawers beneath apparatus are planned and divided for glassware and solvent used in this determination

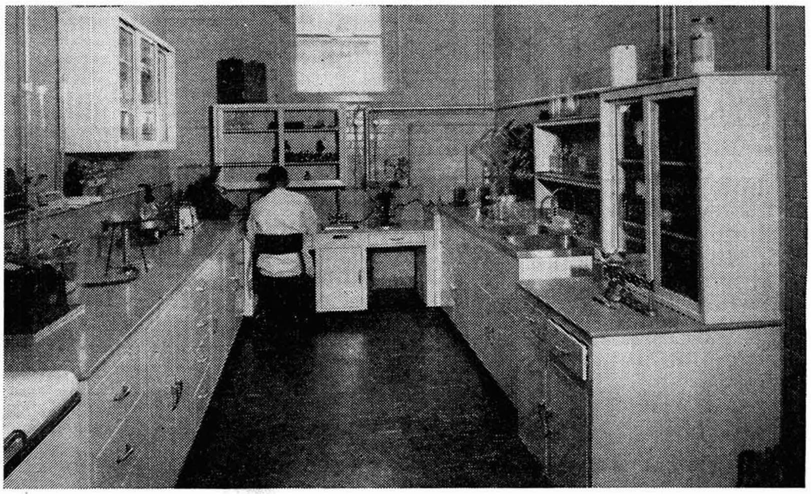


General wash-up sink is of stoneware and has two stainless steel drainboards and two peg boards. Maple top table in foreground is on lock casters. Laboratory personnel tell us it is used for everything from dissections to a place for lunch

Hood is 8 ft., open type, and equipped for the determinations anticipated. Corner is used by dairy control chemist and has large stainless steel sink and general work table



An adjacent room has been equipped as a bacteriology laboratory. Features include a stainless sink, ample instrument and storage space, and a special table for microscopic work

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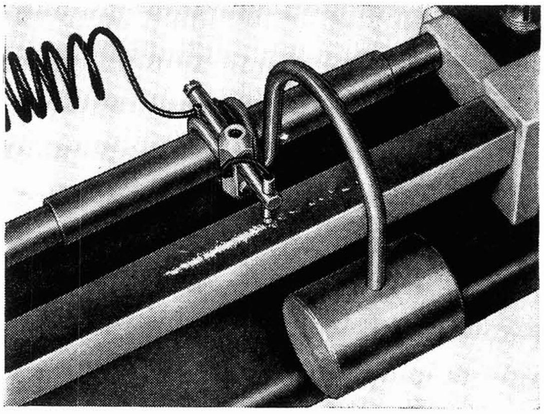

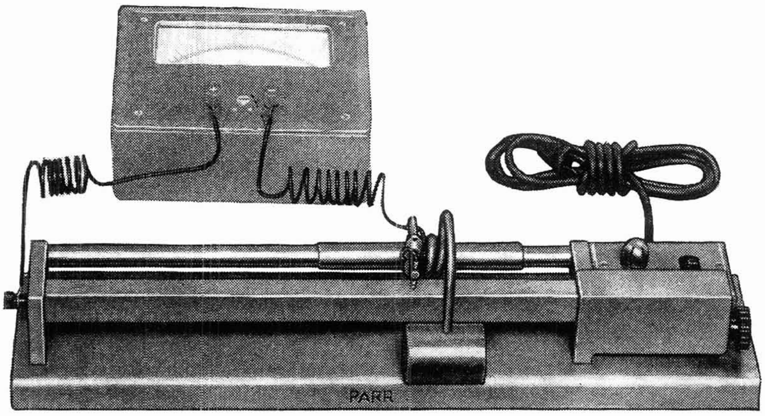
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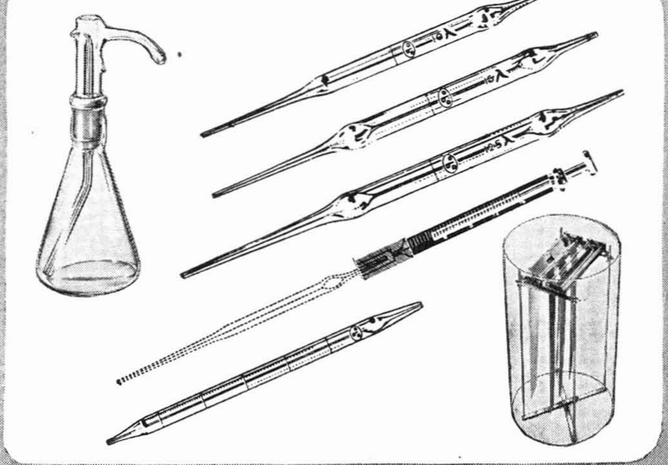

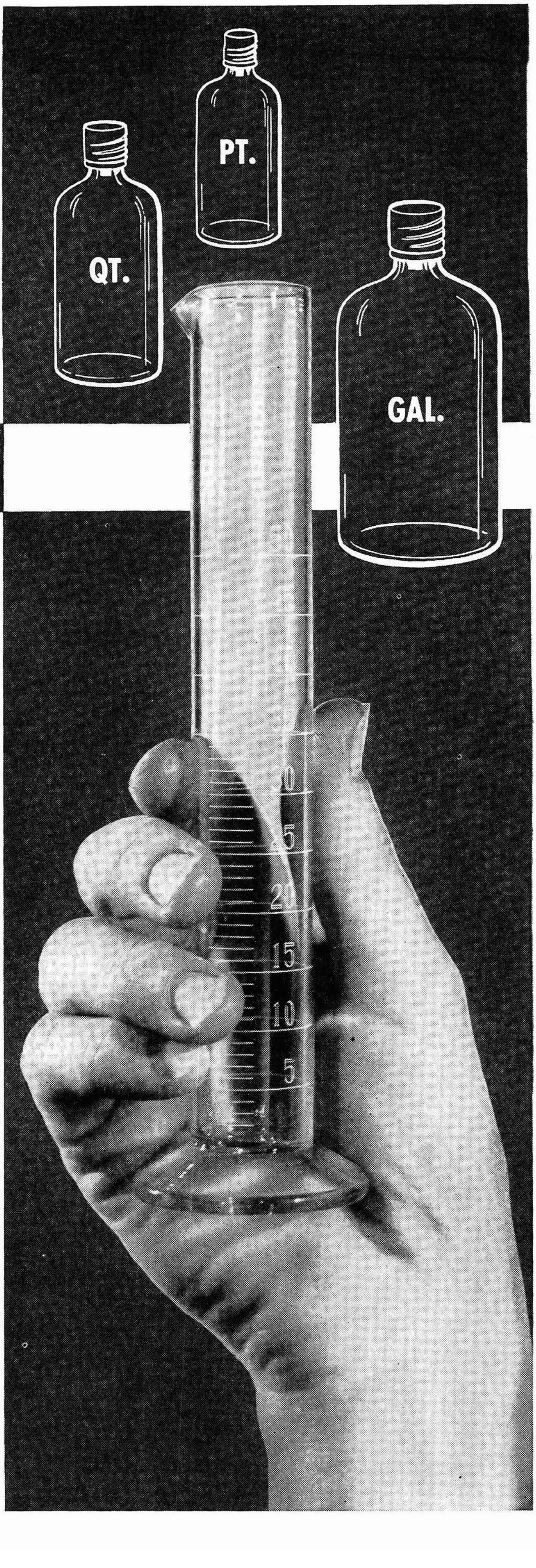
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INSTRUMENTATION

New transistors, multivibrator circuits, oscillators, stepping switches, and vacuum tube voltmeters hold promise of widespread use in analytical chemistry

by Ralph H. Müller

Of the countless advances in new tubes, circuits, and applications thereof, an attempt is made to describe some selected developments which seem to hold promise of rather widespread application in analytical chemistry.

In the past, smooth control of the anode current has required the phase shift method of control. The development of the Plasmatron by RCA laboratories is described by E. O. Johnson of RCA [*Electronics*, **24**, 107 (1951)]. This developmental tube achieves smooth control as an inherent tube property, rather than circuitwise. The Plasmatron is a hot-cathode helium-filled diode capable of controlling large currents continuously at low voltages. A small current of 12 ma. yields an anode current of 950 ma. at an applied anode potential of only 6 volts. The dynamic response is high. The gain is a function of frequency, and is constant and equal to the steady or d.c. gain up to 2 or 3 kc. At 10 kc., it is still 83% of maximum and appears to drop off rapidly above that value, to attain about 50% at 20 kc. The plasmatron will undoubtedly attain widespread use in control and measuring circuits.

Transistor Theory and Practice

Progress in transistor theory and practice is no longer a matter of reference to isolated publications. The November 1952 *Proceedings of the Institute of Radio Engineers* contains 48 original articles, an editorial, and three general commentaries on the present status of transistor theory, devices, and applications. This is little short of a monograph on this subject. Two of these contributions cannot fail to be of interest to the analytical chemist.

K. Lehovec [*Proc. Inst. Radio Engrs.*, **40,** 1407 (1952)] deals with new photoelectric devices utilizing carrier injection. This paper discusses the detection of injected carriers by their absorption and emission due to their recombination with majority carriers. On the basis of this principle, two new components are offered for consideration: a photomodulator which allows the modulation of a light beam by the variation in absorption because of injected carriers; and the "graded seal junction" which permits the light to be transmitted to and from a P-N junction without substantial absorption in the bulk semiconductor. It is likely that the photomodulator combined with a phototransistor may be useful as an amplifier.

A "perfect" photocell is the topic of another of these papers [Shive, J. N., *Proc. Inst. Radio Engrs.*, **40,** 1410 (1952)], which deals with the properties of the M-1740 P-N junction photocell. This new phototransistor employs a special P-N junction and has a sensitivity of 30 ma. per lumen for light of 2400° K. color temperature. This corresponds to a quantum yield (electrons per incident photon) of approximately unity in the spectral range from the visible to the long-wave cutoff at 1.8 microns. This enormous intrinsic sensitivity is not to be confused with the performance of photomultiplier tubes, because the latter owe their high gain to internal amplification by a secondary electron emission process. The new photocell element is encapsulated in a $^{1}/_{4} \times {}^{3}/_{16} \times {}^{3}/_{8}$ inch plastic housing.

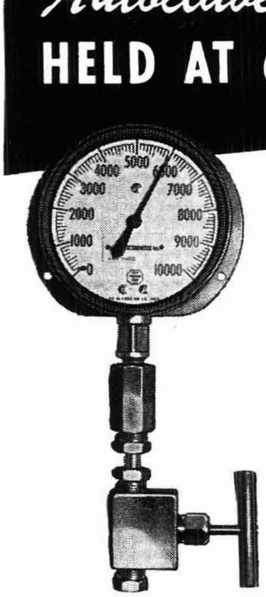
Space is not available for a systematic review of transistor theory and practice. However, a thorough review of this subject and its implications is urgent, and the analyst will need such information very soon.

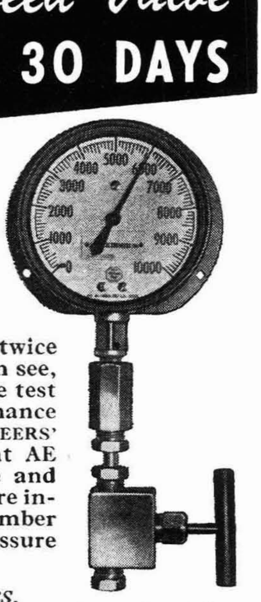
Modern techniques in electrodeposition and coulometric analysis require d.c. sources of great constancy, and many electronic schemes for this purpose have been described. One of these, by J. K. Taylor [*Rev. Sci. Instr.*, **22,** 484 (1951)], furnishes highly regulated low voltages at rather heavy currents. This particular design employs a novel principle. A relaxation oscillator of controllable period feeds pulses of constant amplitude to a power amplifier and rectifier stage. The output voltage is balanced against a reference voltage and the resultant error signal is fed back regeneratively to control the pulse repetition rate.

Multivibrator Circuits

Multivibrator circuits have been used for a long time for precise switching operations, but usually for milli- or microsecond intervals. Two recent developments have extended their usefulness to a range of seconds or even minutes. In one of these, by H. L. Armstrong [*Electronics,* **26,** No. 9, 202 (1953)], two gas triodes use an RC circuit to control the firing cycle of each gas tube. A relay is actuated by the firing of one triode and switches itself to the action of the second triode which, upon firing, in its turn releases the relay and starts the cycle of operations over again. Only one set of contacts on the relay is required for the cycling operation, so that if a D.P.D.T. relay is employed, the extra pair of contacts can operate external control or timing operations. Like the ordinary multivibrator, this circuit can be arranged in a stable, monostable, and bistable form.

A related technique was developed by J. K. Merlis and J. Degelman [*Science,* **114,** 692 (1951)] for an artificial respirator for animal experimentation. This useful device affords an automatic instrument for





INSTRUMENTATION

alternately admitting air or other gases to a system and connecting the system to exhaust at rates varying between 5 and 40 cycles per minute. A double-ended piston in the pump is driven by solenoids. The latter are excited alternately by rectified a.c. which is switched to the solenoids by a relay. The relay is in the anode circuit of a 6J5 tube, which is controlled by the output pulses from a controlled multivibrator. Rate stabilization is obtained by an OD3 voltage regulator tube. A modification is suggested by the authors, in which two 6L6 power tubes can be controlled by the multivibrator to drive the solenoids directly and thus dispense with the relay.

Further developments in vacuum tube voltmeters are concerned with attempts to increase stability, raise the input impedance, and lower the input capacitance. The most recent improvement in this direction, described by A. W. Brewer of the Clarendon Laboratory in Oxford [*J. Sci. Instr.*, **30**, No. 3, 91 (1953)], utilizes an electrometer tube in conjunction with an ordinary pentode or triode, both acting as cathode followers. A voltage gain of 0.90 is attained with input leakage current of the order of 10^{-14} A. and input capacitance which is a small fraction of 1 microfarad. By the further addition of two pentodes acting as "tail tubes," the input range can be extended to ±500 volts, although a power supply of 1200 volts is required for this range. The power dissipated by the second tube is great enough to operate an ordinary voltmeter or recorder.

Another logarithmic amplifier extending over a range of 1 to 10^5 has been described by M. Briere, A. Rogozinski, and J. Weill [*J. phys. radium,* **12**, 144 (1951)]. It has been known for a long time that a logarithmic relation exists between the current through a diode and its anode voltage when the latter is negative. This phenomenon has been reinvestigated in the region of very weak currents. A circuit is described using a multigrid electrometer tube in diode connection, and operated at subnominal rating. It is fed from various sources such as ionization chambers or phototubes. The logarithmic portion of the current-voltage curve extends over five decades. The lower limit depends upon the tube, but in some cases currents as small as 10^{-14} A. follow this relationship. The importance of logarithmic elements or circuit is much greater than one might suspect, because they enter into several of the prevailing methods for high-speed multiplication in which logarithmic terms are fed into summing or difference amplifiers.

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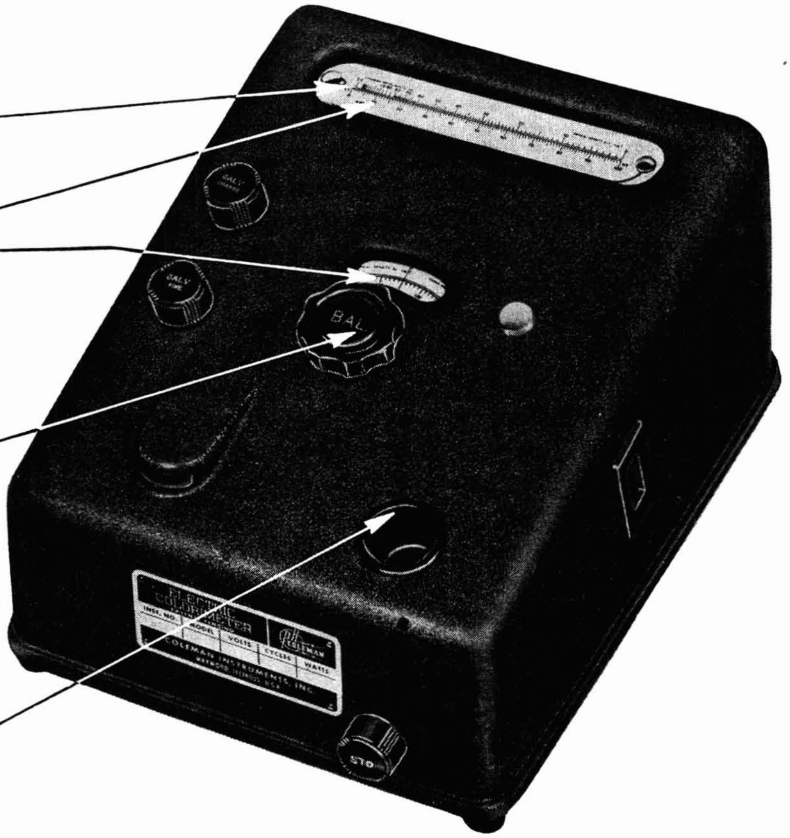

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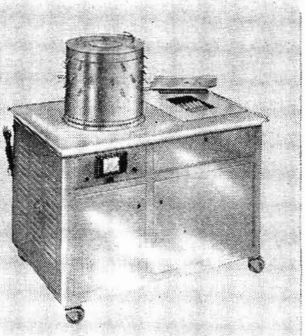

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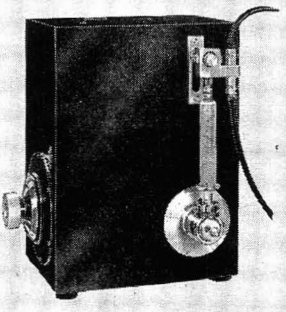

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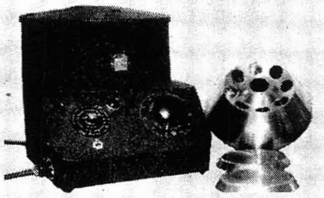

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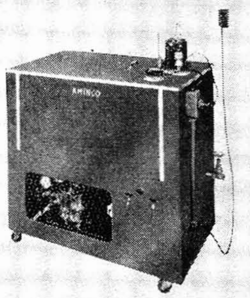

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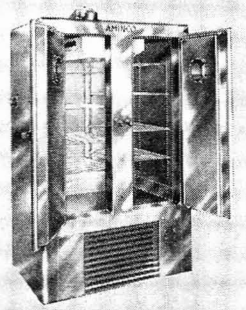

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is an ancient principle first treated by Gouy. It has been used rather frequently in recent years as a means of reducing stiction errors in meters and recorders. A very thorough treatment of the subject by R. L. Ives [*Electronics*, **25**, 161 (1952)] is particularly useful because it is concerned with a discussion of long-term reliability of such devices. Relay oscillators with a frequency of 5 to 15 cycles are so successful that they are being incorporated into all modern field meteorological instruments. However, for fixed station operation, their life is too short. A good telephone-type relay is dependable for 10,000,000 operations. At 10 cycles per second on 24-hour operation, this is used up in about 11.6 days A line-operated keep-alive circuit employing a 10-cycle multivibrator will yield 40 days of continuous service with ordinary tubes. When red tubes (10,000 hours) are used, monthly checking is advisable and tube replacement is indicated every 13 months. This study has shown that the keep-alive frequency injected into the measuring circuit should be between 5 and 15 cycles per second and that the wave form should be nonsinusoidal but symmetrical. Frequencies of less than 5 cycles per second require excessive amplitude to be effective and insert sawteeth into the record. Frequencies of much more than 15 cycles per second interfere with ink flow in pens of several designs, converting the recorder into a very efficient ink thrower. Frequencies in excess of 400 cycles per second make continuous excavations in the chart.

Stepping Switches

There would seem to be little possibility for further improvement in stepping switches. These have attained a high degree of development in the form of the multiple bank selector switch commonly used in automatic telephone exchanges. However, new designs have been forthcoming from several sources. One of these is the new Roto-Stepper manufactured by the G. M. Giannini Co., Pasadena, Calif. This device, which weighs less than 1 pound, is capable of unlimited clockwise or counterclockwise rotation. It is solenoid-operated with a normal increment of 2°. It operates at 24 volts, 0.6 ampere maximum, and can be ordered in various combinations with or without shaft output. Some of these are: shaft output with potentiometer output, shaft output with potentiometer output and homing segments, and the same plus internal autocycling. With a minimum pulse length of 0.05 second, the maximum stepping rate is 720 per minute. This can be raised to 30 per second, depending on torque. The torque output varies with the pulse rate, but is approximately 12 inch-ounces at 12 pulses per second.


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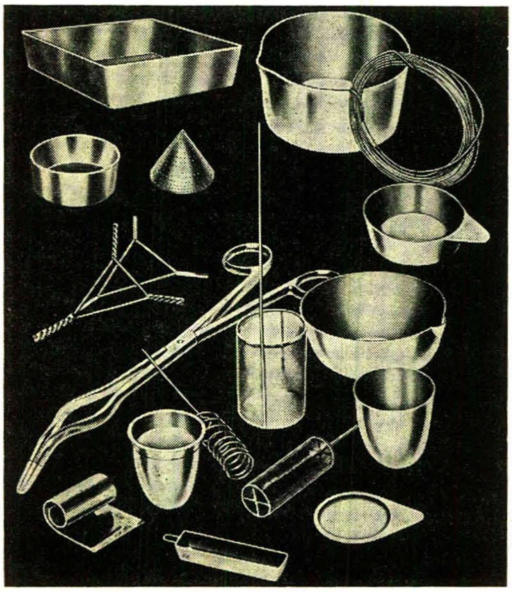

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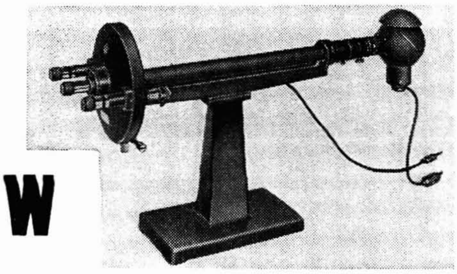

NEW

Lippich Type Polarimeter

(Schmidt & Haensch)

A precision instrument for measuring the rotation of the plane of polarization of all optically active substances. Big advantage is its glass circle instead of a metal circle. The scale on glass, instead of on metal, in conjunction with a micrometer plate, permits direct reading without vernier, resulting in greater speed and precision of reading. Glass circle is rigidly connected with the analyzer and carries two scales, an angular scale in degrees arc, and a scale in international sugar degrees. Sodium vapor lamp is an integral part of the instrument and is always in alignment and ready for use.

Model A with receiving trough for tubes up to a length of 220 mm.
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Bulletin SH-344 on request

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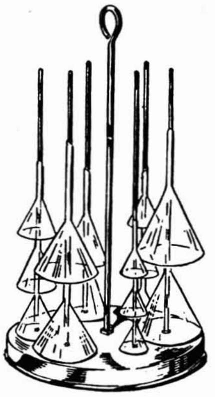
DWORECKI

FUNNEL STACKRACK

Holds Funnels From 1½ ins. to 3 ins. in Diam.



The Dworecki funnel rack consists of a stainless steel base 10½ in. in diameter by ⅞ in. high, 6 steel support rods 14¾ ins. high by ⅛ in. in diameter for holding funnels, and a center rod 18″ high by ¼ in. in diameter with a 2½ in. ring at the top for carrying.

ADJUSTABLE

The base contains 10 holes permitting the rods to be fastened on different centers to accomodate various size funnels up to 3 ins. in diameter.

CAPACITY

The Dworecki funnel rack will hold up to 40 funnels depending upon the size and length of stem.

CONVENIENT

Up to forty clean unnels are slipped over the support rods and are held ready for instant use. Reduces the danger of breakage by rolling off of tables or shelves.

PORTABLE

As an added convenience, use two Dworecki funnel racks—one for clean funnels—one for used funnels. Racks with funnels can be carried as a unit to the wash sink.

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One of a wide line of highly-dependable hot plates, this NEW TEMCO Model 2500 is the finest money can buy in its comparable size range. Top quality throughout, it combines the best in performance plus excellent appearance. Extra sensitive thermostat provides stepless control with less than 3° variation at any point from room temperature to 370° C. (700° F.). Machined smooth cast aluminum surface plate reaches top temperature in 25 minutes, has negligible temperature gradient. Interior of case and your table top protected from heat by scientifically designed ventilating channels. Long, spiraled heating element embedded in refractory plate, replaceable without new surface plate. Dovetail sockets at rear for holding apparatus. $27.50. Write for data and name of nearest dealer.

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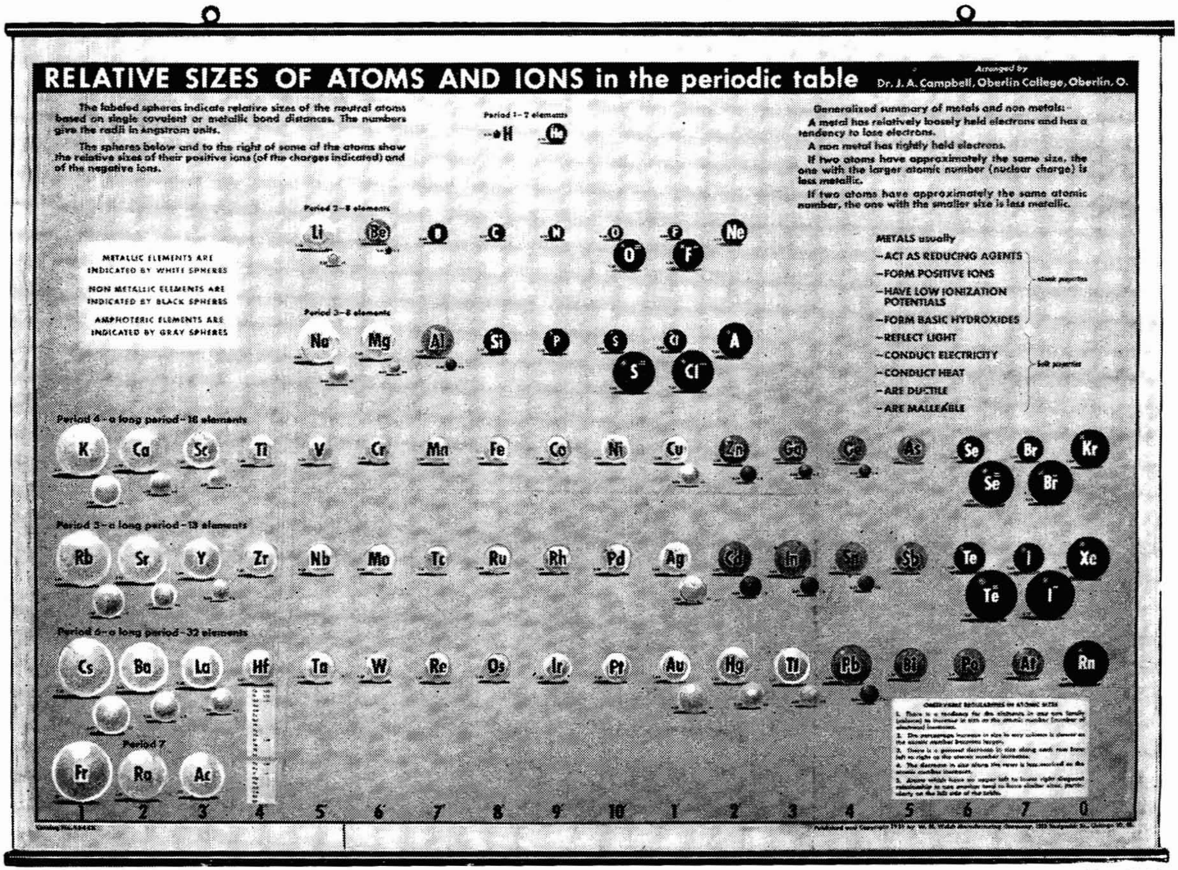
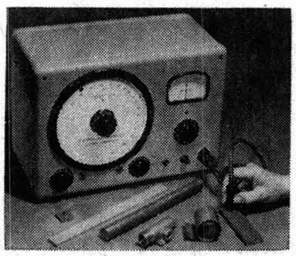

RELATIVE SIZES OF ATOMS AND IONS in the periodic table
Arranged by Dr. J. A. Campbell, Oberlin College, Oberlin, O.
The labeled spheres indicate relative sizes of the neutral atoms based on single covalent or metallic bond distances. The numbers give the radii in Angstrom units.
The spheres below and to the right of some of the atoms show the relative sizes of their positive ions (of the charges indicated) and of the negative ions.
Period 1 – 2 elements
H
He
Generalized summary of metals and non metals:–
A metal has relatively loosely held electrons and has a tendency to lose electrons.
A non metal has tightly held electrons.
If two atoms have approximately the same size, the one with the larger atomic number (nuclear charge) is less metallic.
If two atoms have approximately the same atomic number, the one with the smaller size is less metallic.
METALLIC ELEMENTS ARE INDICATED BY WHITE SPHERES
NON METALLIC ELEMENTS ARE INDICATED BY BLACK SPHERES
AMPHOTERIC ELEMENTS ARE INDICATED BY GRAY SPHERES
Period 2 – 8 elements
Li Be B C N O F Ne
O F
Period 3 – 8 elements
Na Mg Al Si P S Cl A
S Cl
METALS usually
–ACT AS REDUCING AGENTS
–FORM POSITIVE IONS
–HAVE LOW IONIZATION POTENTIALS
–FORM BASIC HYDROXIDES
–REFLECT LIGHT
–CONDUCT ELECTRICITY
–CONDUCT HEAT
–ARE DUCTILE
–ARE MALLEABLE
Period 4 – a long period – 18 elements
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Se Br
Period 5 – a long period – 18 elements
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Te I
Period 6 – a long period – 32 elements
Cs Ba La Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
Period 7
Fr Ra Ac
1 2 3 4 5 6 7 8 9 10 1 2 3 4 5 6 7 0

NEW PRODUCTS FOR ANALYSTS

Equipment, Apparatus, Instruments, Reagents, Materials

Conductivity Meter

Rapid nondestructive testing of nonferrous conducting materials is possible with the Magnatest FM-100 instrument brought out by Magnaflux Corp. The large dial on front of the meter shows absolute conductivity measurement when the operator places the hand probe on a metal surface. A relatively flat area of about $^3/_8$ inch in diameter is all that is required on which to place the probe; wirelike samples or cross sectioning of parts is not necessary.



Conductivity readings with the instrument can be used to sort mixed lots of metals and alloys. Or the relationship between conductivity and other properties can be used to evaluate hardness or to control heat treatment or purity of melt with samples of nonmagnetic metals. **1**

Radioactivity Counting System

Equipment for the Bernstein-Ballentine counting system for measuring carbon-14 activity in the gaseous phase is being distributed by The Atomic Center for Instruments & Equipment, Inc. This consists of a 100-ml. gas phase proportional counter, a calibrator for determining the counting sensitive volume, a freezing coil for trapping water vapor, and a methane reservoir, all made of borosilicate glass. A scaling unit is also needed.

The general method used consists of transferring a known volume of radioactive carbon dioxide to a gas phase Bernstein-Ballentine proportional counter of known counting volume. Sample weights of 0.1 to 15 mg. of carbon can be used. The counting rate is proportional to the sample weight. **2**

Temperature Controller

A stepless temperature controller is being produced by West Instrument Co. The unit contains no relay and supplies only enough power to the heating element to hold the temperature for which it is set. Full power operation is only during the initial temperature rise.

The controller is made up of two sections. One contains a temperature indicator, two pilot lights, and part of the control circuit. The heavier parts of the circuit are in the other section. The indicator section may be panel-mounted. Models are available to handle loads from 300 volt-amperes to 110 kilovolt-amperes. **3**

Relay

E. H. Sargent & Co. has redesigned its laboratory relay for general use where an electrical switching device with low power and high impedance input requirements is desired. The relay is capable of handling substantial power loads with minute currents through the contacts of regulating devices used in conjunction with it. A time delay of one to two seconds is incorporated into the circuit, minimizing chatter without loss of sensitivity.

The electrical circuit is isolated from the line by a transformer, and a grounding lead is provided with the line cord to eliminate the possibility of electrical shocks to the operator or erratic operation when used with constant temperature baths having exposed heaters. Two electrical outlets are located on the

Circle desired items for further information on items listed in this section

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Manufacturers' Literature 21 22 23 24 25 26 27 28 29
30 31 32 33 34 35 36 37 38 39 40

Name____________________Position____________

Company____________________________

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front panel of the relay case. Each outlet—one energized when the regulator closes, the other operating inversely—is capable of supplying 10 amperes. A pilot light and a line switch are also located on the front panel. **4**

Differential Colorimeter

The Colormaster differential colorimeter of Manufacturers Engineering & Equipment Corp. is suitable for color measurements of synthetic fibers, paints, solutions, pigments, slurries, and other substances. The manufacturer reports that a complete set of color measurements can be made in less than 30 seconds.

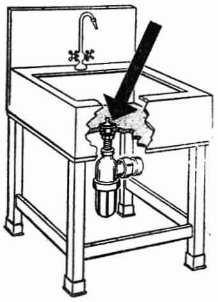
Three color filters give approximations to the ICI X, Y, and Z functions. Transmissions and reflections are measured directly. The linearity of the instrument is within approximately 0.2% reflectance or transmission down to 10%; standardization on a dark panel permits extension of the range. The dial can be read to 0.1%. **5**

Scaler

A scaler for use with Geiger or scintillation counters has been announced by Nuclear Instrument & Chemical Corp. The Model 183 instrument is designed for routine sample counting and features controls to allow operation for a predetermined number of counts or a predetermined length of time. It can be used in conjunction with a sample changer for automatic counting of up to 50 radioactive samples.

Higinbotham scale of 256 and 2-microsecond resolving time permits counting samples of high activity. A built-in timer indicates elapsed time to 9999.99 minutes and an internal high voltage supply provides 500 to 2500 volts for Geiger or scintillation detectors. A single switch operates electrical reset of register, timer, and interpolation lamps. The unit may be obtained without the timer and with manual reset controls. **6**

Sink Unit



An unbreakable, chemical resistant laboratory sink unit made of polyethylene has been announced by Arthur S. LaPine & Co. This Lanco unit consists of stopper, high level drain, strainer, lock nut, plug, trap, and outlet union. It can be quickly removed, cleaned, and replaced without the aid of tools. Polyethylene construction makes it resistant to acids, alkalies, and other corrosive materials, as well as offering physical toughness. **7**

Aluminum Fluoride

Aluminum fluoride has been added to the reagent line of Fisher Scientific Co. for use in catalyst studies with hydrocarbons. Specifications of the material: maximum of 0.005% chloride, 0.001% sulfate, 0.008% iron. It is offered in $^1/_4$-, 1-, and 5-pound quantities. **8**

Microbalance

A single-pan microbalance of 20-gram capacity for rapid weighings with an accuracy of ±0.002 mg. is being sold by Fisher Scientific Co. Similar in features to Fisher's larger scale Gram-atic balances, the Micro Gram-atic balance has two knife edges instead of three and automatically registering weights which are mechanically removed by dialing on the front panel.

Original sensitivity of the instrument is high and, as all weighings are made under a constant load, sensitivity remains constant throughout the weight range of the balance. Weighings can be completed within 35 seconds, according to the manufacturer.

Operation is simple. A sample is placed on the pans and weights are removed

(*Continued on page 44 A*)

These handy return cards will bring information of use to chemists and engineers in laboratory, pilot plant, and production. The items listed in this special section have been selected by the editors of ANALYTICAL CHEMISTRY for their value and timeliness in helping you to keep abreast of the latest developments in the field.

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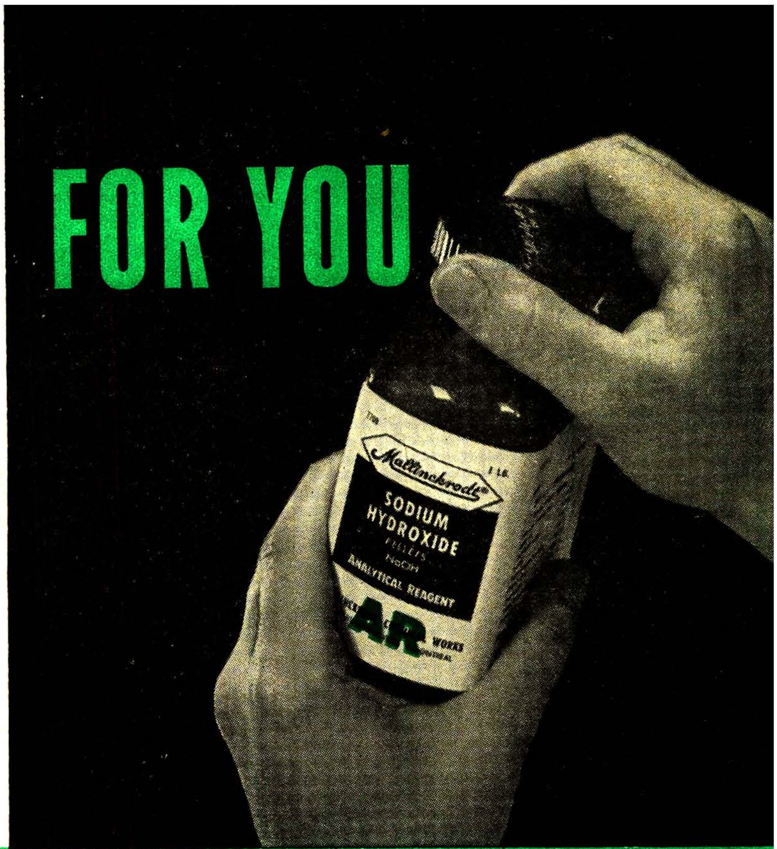
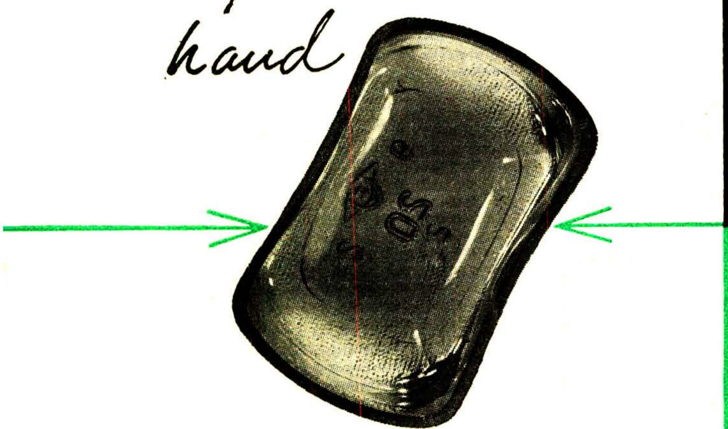


the Concave Sides fit your hand



For many months, Mallinckrodt worked with glass industry engineers to perfect the STORMOR bottle. That's why it's far more than just a new package design – it's a specialized container engineered to make it easier for you to use Analytical Reagents.

"It is the most helpful advance in reagent packaging in many years," was the reply when Mallinckrodt checked independent chemists who used AR's in STORMORs. They liked the feel of the bottle's concave sides, and they appreciated the space it saved. Its modern appearance in the laboratory pleased them, and they thought the new label had better visibility.

Today Mallinckrodt AR's in STORMOR bottles (1 lb. and ¼ lb. sizes available, except liquids) are standard laboratory equipment throughout the country. Sharp increases in the number of chemists using AR's leave no doubt of this. Ask your Mallinckrodt dealer for AR's in STORMORs – you'll pay no premium.

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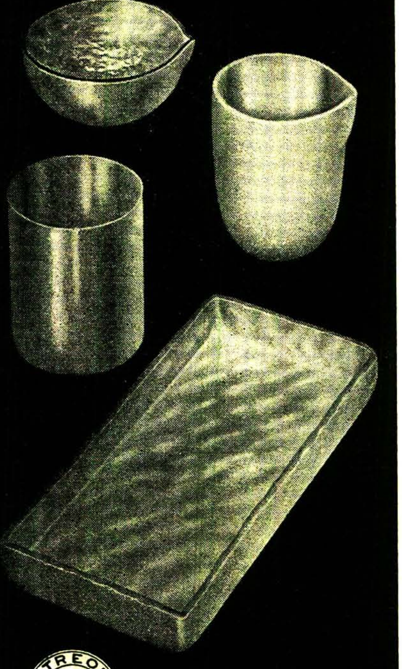


NEW PRODUCTS, continued

by means of knobs on the front panel, down to 0.01 gram of the sample weight. Weights removed are automatically registered on a counter on the panel. The third and fourth decimal places are read from the projection system's ground-glass screen; the fifth and sixth decimal places are obtained by turning an optical micrometer. An effective air damper stops oscillations quickly for readings.

The body of the balance has a metal front shield to protect the instrument from the operator's body heat. The entire unit is finished in white enamel for optimum heat reflectance. **9**

Laboratory Evaporator

A device for the evaporation of liquids in laboratory work has been developed by Quartz Products Corp. The Epiradiator subjects the surface of the liquid to calorific radiation, instead of inducing evaporation by boiling. Energy absorbed by the surface layer produces evaporation while the remainder of the liquid and the vessel itself remain relatively cool. This technique results in a clean residue, no boil over, and rapid operation.

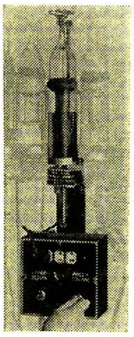
Manufactured of fused silica, the Epiradiator is offered in four sizes for operation on 110 or 220 volts. **10**

X-Ray Spectrograph Attachment

An attachment which permits use of helium instead of air in the path of the x-ray beam of x-ray spectrograph units is available from North American Philips Co., Inc., for use on Norelco instruments. The helium atmosphere extends the useful spectrum range of the x-ray analysis equipment at least down to sulfur. Data obtained with the unit, says North American Philips, indicate a probable sensitivity limit of 0.02% for sulfur, with comparable sensitivity limits for other elements in the same atomic range.

Accessory equipment includes a housing that encloses the x-ray tube and provides a compartment for the specimen holder, a plate-type collimator with mounting, and an accordion-shaped rubber jacket that encloses the analyzing crystal and connects the specimen compartment to the Geiger tube collimator assembly. The rubber jacket has a port for attachment of the helium supply tube. **11**

Gas Analysis Apparatus



Fisher Scientific Co. has introduced a standardized absorption apparatus for gas trains which, it claims, can more than double the gas analyst's work output. The automatic Fisher-Reeder pipet is mounted in an absorption train. A switch actuates a solenoid-driven pump which injects four jets of absorbent chemical into the pipet's gas-filled chamber 24 times per minute. The gas itself is agitated for thorough mixing.

After transfer, another component of the sample is absorbed in a second pipet, then in a third, and so on, depending on the size of the operation. Any number of units can be used in the absorption train by plugging them into control boxes in groups of three. The analyst is free to run several absorption units or to perform some other task while the pipet operates automatically.

The apparatus is said to offer improved reproducibility. Determinations on aliquots of the same sample can be duplicated merely by repeating the time in which gas and fresh absorbent are in contact. **12**

Carbon Dioxide Analyzer

A portable instrument for flue gas analysis with small boilers and heaters has been developed by Thermco Laboratories. The analyzer draws a sample of gas from the flue and pumps it into a thermal conductivity cell. Carbon dioxide content is measured continuously on a meter.

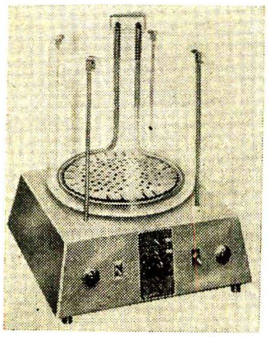
Readings change within 5 seconds after a change has occurred in the flue gas composition. The indicator's range is from 0 to 20% and it is accurate to $^{1}/_{4}$%. **13**

Water Bath

A jar bath being marketed by Blue M Electric Co. provides automatic, efficient agitation without use of motors, stirrers, or circulating systems by means of the pulsation of a perforated agitator plate. The plate is pulsated by an elec-

For further information, see coupon on page 41 A

tromagnet located in the base support and actuated by a selenium rectifier, capacitor, and timed relay with cadmium contacts. Full visibility and maximum utilization of work space are attained.



The equipment's temperature control permits automatic selection of the two most used temperatures within the range of the bath. Other temperatures can be selected without disturbing the two preselected temperature settings. Sensitivity of the temperature control is ±0.1° C.

The Magni-Whirl jar bath is available in two temperature ranges—ambient to 70° C. and ambient to 100° C.—and three standard sizes of borosilicate glass jars. **14**

Antifoam Spray

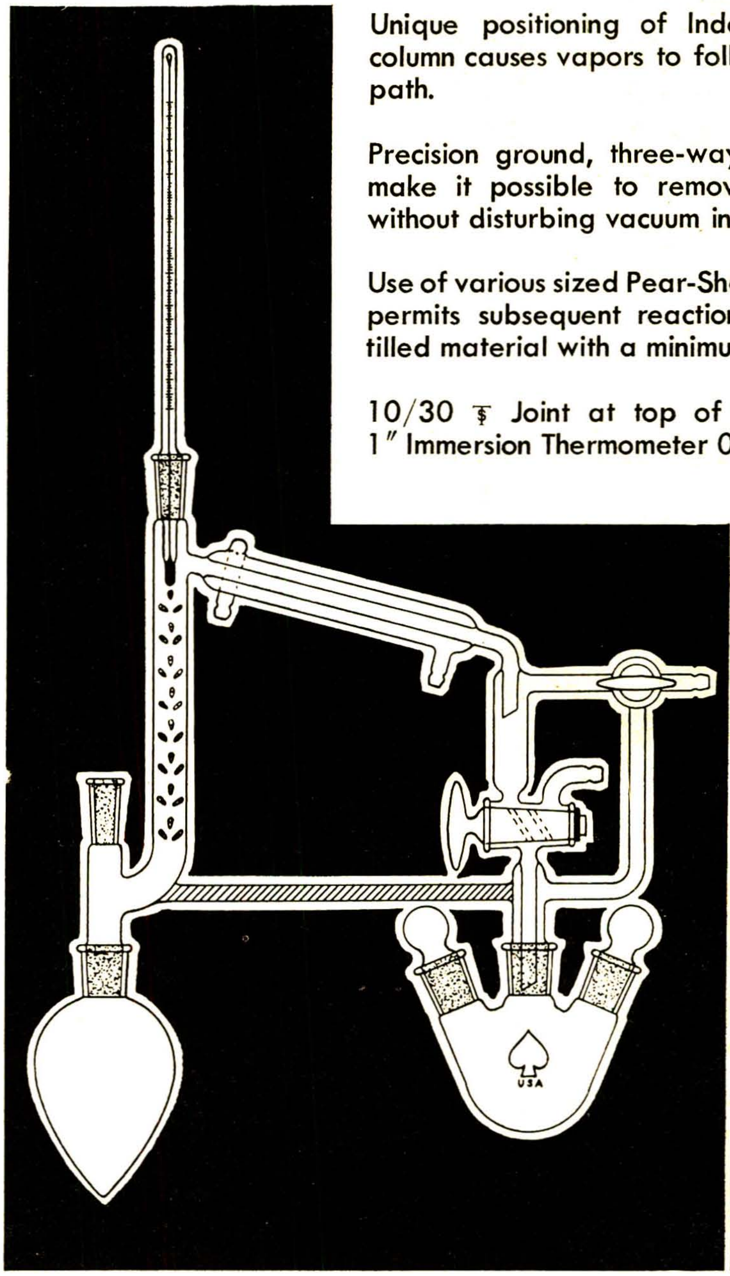
An aerosol-packaged dispersion of silicone compound in Freon, Dow Corning Corp.'s Antifoam A Spray gives rapid foam control in laboratory or other small-scale operations. A foam-killing mist blankets the foaming material at the touch of a valve, eliminating the need for preliminary measuring and mixing of the antifoam agent in the foaming material and the possibility of over-application.

Effective concentrations of silicone usually range from 0.01 to 1.0 part per million, and in most cases no trace can be detected in the finished batch after defoaming. The volatile Freon propellent vaporizes harmlessly upon discharge. **15**

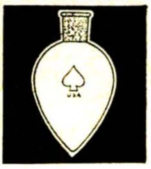
Analog Computers

Two new desk-top electronic analog computers are in production at Reeves Instrument Co. The units can solve differential equations or simulate physical systems up to the sixth order of magnitude. All mathematical operations are performed with better than 0.1% accuracy. The computers measure 20 × 25 × 20 inches.

The models are self-contained, with built-in supplies for amplifier and relay

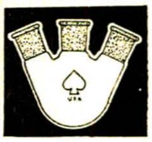


6968
Pear Shaped
14/20 Joint
Capacities:
10-25-50-100-250 ml



6886
Round Bottom
14/20 Joint
Capacities:
10-25-50-100-250 ml

6963
Three Neck
Round Bottom
14/20 Joint
Capacities:
50-100-250 ml



NEW PRODUCTS, continued

operation and an internal computing reference source. Problems are set up on patch boards which plug into the front of the computer, so that one instrument can be used for several problems with minimum set-up time. External equipment can be wired into problems through binding posts and connectors, permitting a desk-top computer to be interconnected with other computers of any size.

Model C301 has all components wired directly to the patch bay for flexibility. Problem control is obtained by patching computing elements through switches and relays.

Model C302 has an integrated internal problem control system. Patching and operating of problems is the same as in Reeves' larger computers. **16**

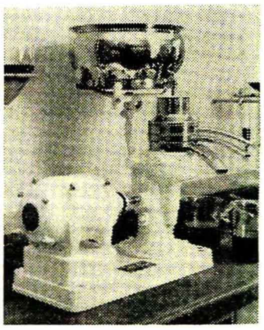
Electrophoresis Unit

A paper electrophoresis unit for separation, identification, and quantitative determination of such complex systems as mixtures of amino acids, lipides, steroids, carbohydrates, and proteins has been designed by Microchemical Specialties Co. The equipment permits up to 10 analyses to be made simultaneously.

Buffer cells and tray for supporting filter paper are made of clear plastic. Trays of differing length can be used when different lengths of paper are required. One stainless steel and one carbon rod are used as electrodes in the buffer cells. **17**

Centrifuge

A laboratory centrifuge called the Westfalia LWA-205 is being distributed in the United States by Merco Centrifugal Co. The machine is equipped with four interchangeable bowls to provide concentration, liquid clarification, solvent extraction, and centrifugal mixing. Bowls can be fitted quickly onto the same base.



The centrifuge has a capacity of 0.2 to 2 gallons per minute and operates on 110, 220, or 440 volts. Centrifugal speeds up to 12,000 r.p.m. and centrifugal forces of 7500 gravities or more are attained. The unit weighs less than 150 pounds and measures 30 inches high. Internal parts are of stainless steel. **18**

Marking Pen

Tech-Pen is a laboratory marking pen, marketed by Mark-Tex Corp., that will write on glass, metal, wood, porcelain, and other porous and nonporous surfaces with opaque, quick-drying ink. Markings are resistant to temperature changes and many chemicals. They can be removed by use of organic solvents. Various colors of ink are supplied with the metal pens. **19**

Microscope Camera

The Orthophot, an integrated reflex camera and controlled light source for use with any standard microscope, has been brought out by Silge & Kuhne. The camera unit can be swung back when the microscope is to be used visually. A photoelectric light meter facilitates proper exposure, and the reflex viewer and an integral focusing device are claimed to provide precise focusing.

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ture, and size of illuminated field. Built-in color filters are included and provision is made for use of liquid filters. The illuminator may be used for bright-field, dark-field, polarized light, or phase contrast work. Accessories are available for fluorescence microscopy.

The standard Orthophot camera uses roll film for $2^1/_4 \times 2^1/_4$-inch pictures in black and white or color, $2^1/_4 \times 3^1/_4$-inch sheet or pack film, or 35-mm. film. A special unit handles 4×5 inch, $3^1/_4 \times 4^1/_4$ inch, or 35-mm. film. Adaptors are available for use with other cameras. 20

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Radiation Instruments. Catalog of 12 pages covering electronic instruments, accessories, and tubes for nuclear counting applications. Detectolab, Inc. (*Cat. 3A*). 21

Glass Tubing and Pipe. Two bulletins of 4 pages each present specifications for precision-bore tubing and specialties and for glass pipe, stopcocks, and fittings. Fischer & Porter Co. (*Cat. 80-10 and 80-20*). 22

Radiation Instruments. Electronic instruments, counter tubes, glass apparatus, accessories, and materials for radiation detection covered in a catalog of 58 pages. Radiation Counter Laboratories, Inc. (*Cat. 15*). 23

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Stop Watches. Catalog of 12 pages lists types of stop watches and recording chronographs distributed by Herman H. Sticht Co., Inc. (*Minerva Instruments*). 26

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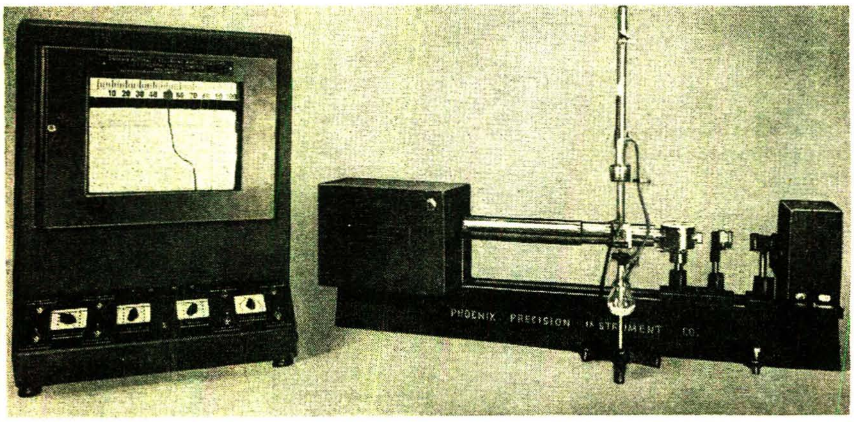

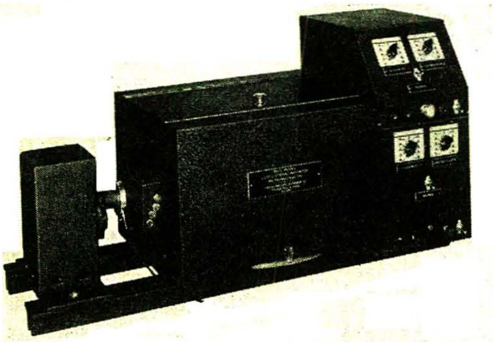

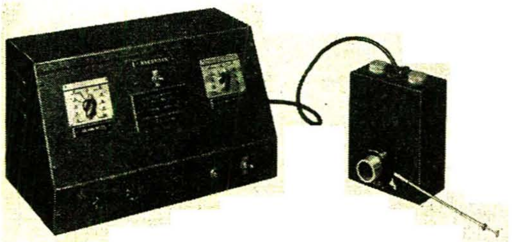

LITERATURE, continued

sheet published by National Safety Council (*Data Sheet D-206*). **29**

Humidity Cabinet. Two-page sheet describes constant temperature and humidity cabinet with capacity of 6 cubic feet. Food Technology, Inc. (*Aire-Regulator*). **30**

Food Analysis. Price list of 4 pages covering mineral, vitamin, amino acid, and miscellaneous analyses and tests of foods and beverages. Raymond C. Crippen Research & Development Laboratories (*Bull. 20*). **31**

Fatty Alcohols. Bulletin covers chemical composition, reactions, applications, and solubility data for line of fatty alcohols produced by Archer-Daniels-Midland Co. (*Tech. Bull. 903-A*). **32**

X-Ray Instruments. Booklet of 64 pages with data on x-ray diffraction, spectrometry, and spectrography instruments, tubes, rectifiers, cameras, and other accessories, as well as electron microscopes, for research and control applications. North American Philips Co., Inc. **33**

Laboratory Furniture. Twelve-page brochure catalogs sectional laboratory furniture fabricated of lead-coated steel and describes construction and assembly. Metalab Equipment Corp. (*Cat. SD-2*). **34**

Frequency Meters. A 2-page sheet describes and lists specifications of various models of frequency meters for field and laboratory use. Frequency Standards. **35**

Xylene and Toluene. Safety data sheet of 3 pages describes hazards and detection of xylene and toluene and personal protection in their use. National Safety Council (*Data Sheet D-204*). **36**

Radiation Instruments. Catalog of x-ray and radiation measuring instruments, dosimeters, and components manufactured by The Victoreen Instrument Co. **37**

Balance Table Construction. Folder describes plans for construction of vibration-free balance tables. Fisher Scientific Co. (*Bull. FS-240*). **38**

High Vacuum Equipment. Price list of 12 pages covering industrial processing equipment, metal and glass pumps, gages, valves, and accessories manufactured by Consolidated Vacuum Corp. **39**

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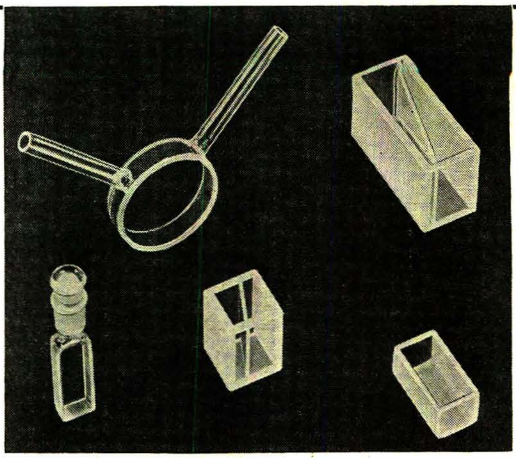

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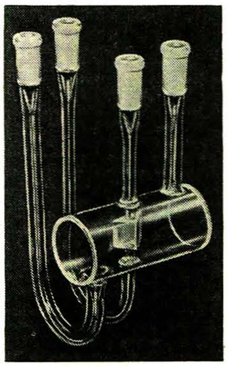

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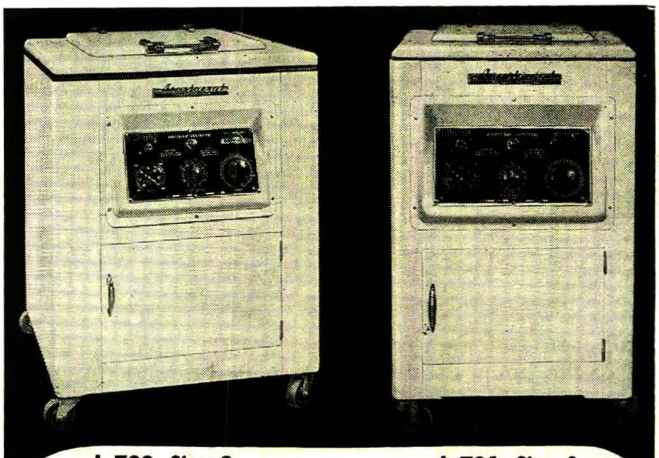

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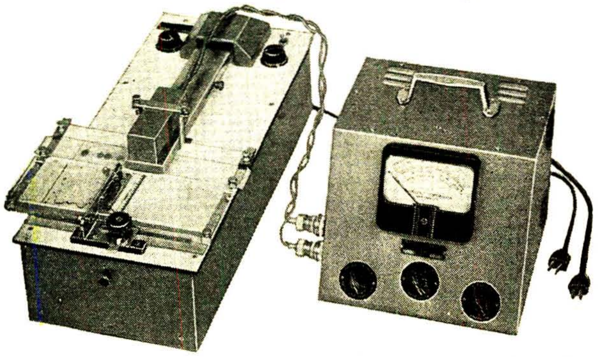

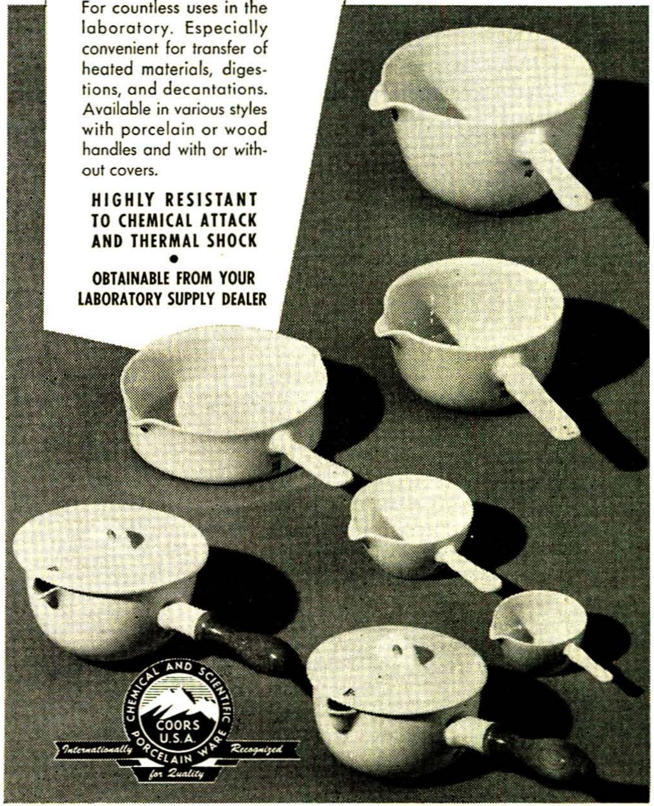

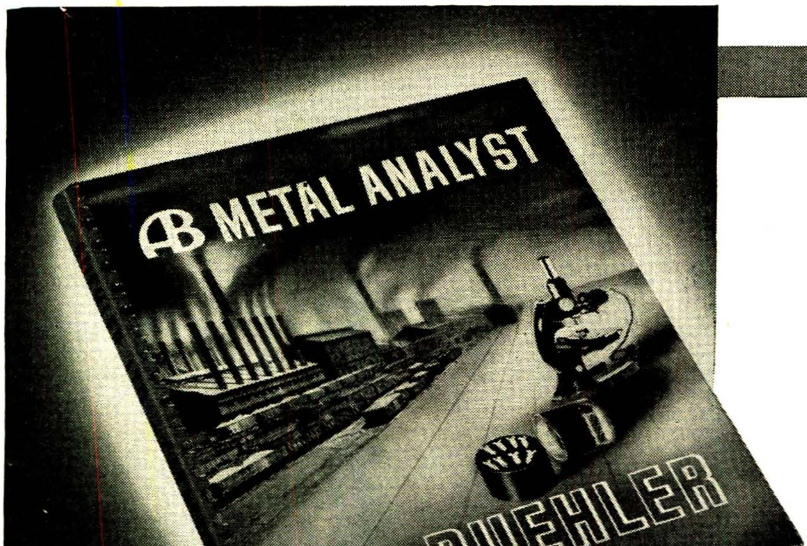
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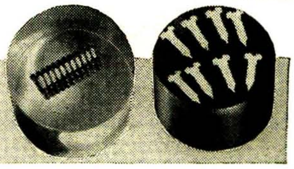

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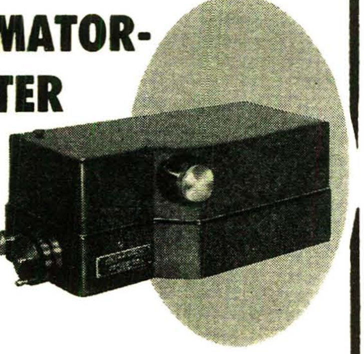

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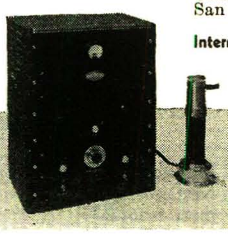

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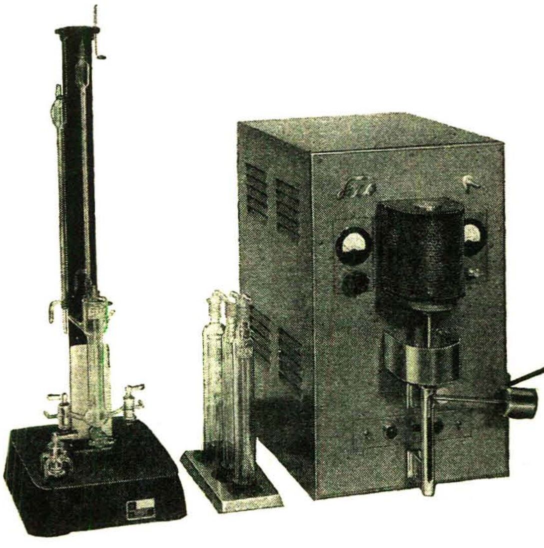

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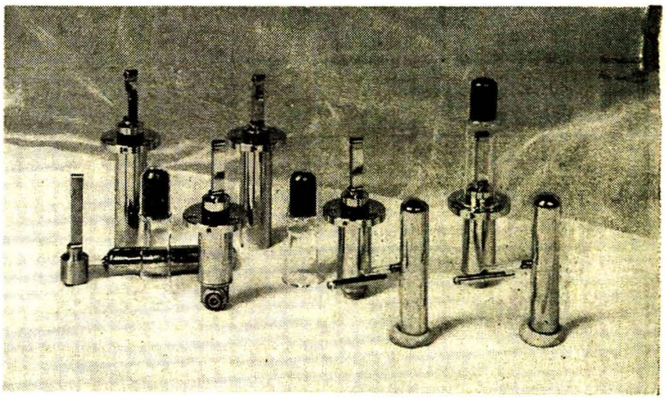

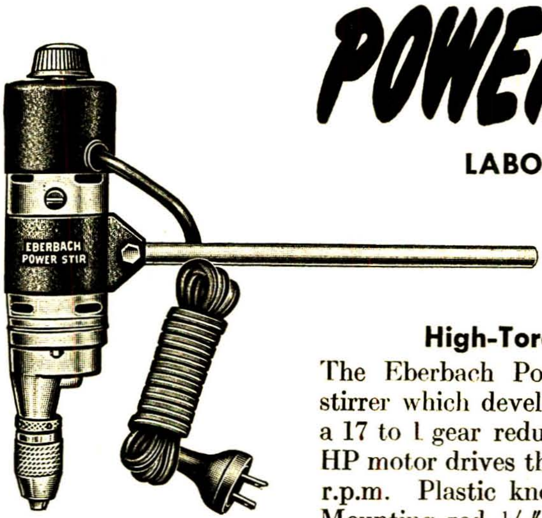
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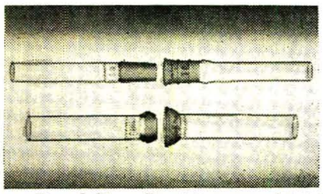

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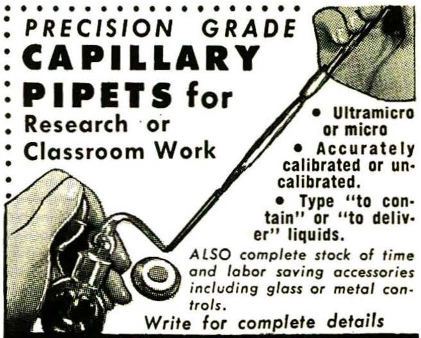

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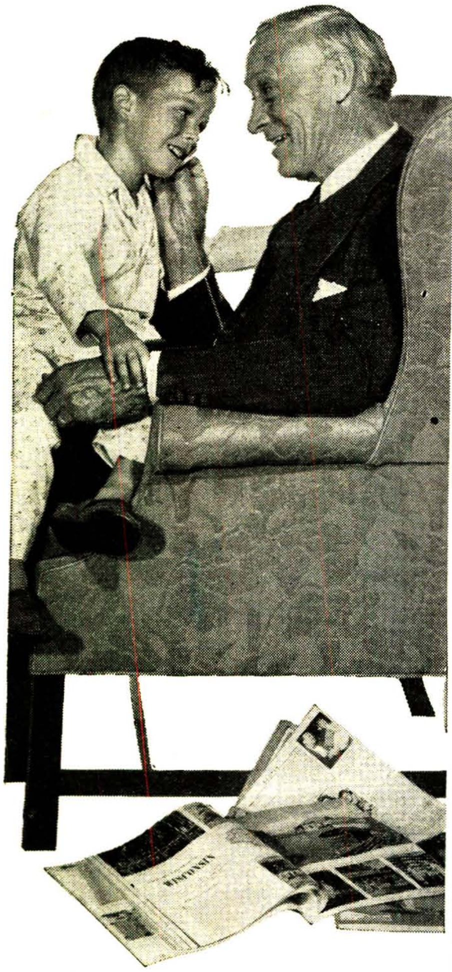

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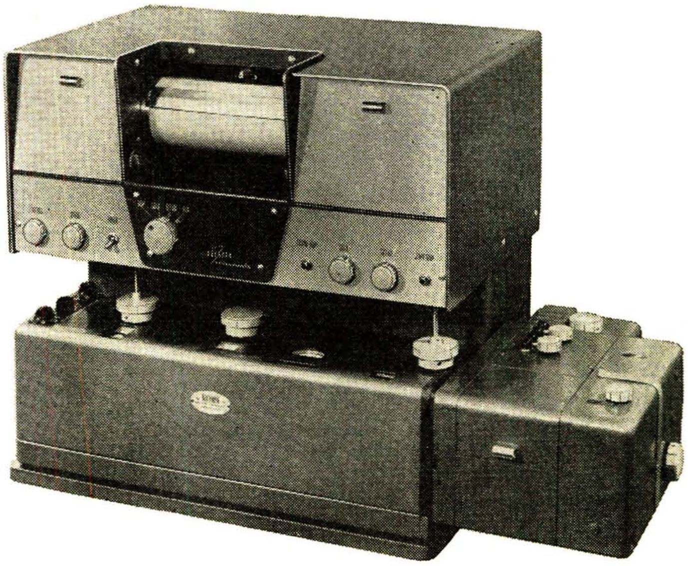

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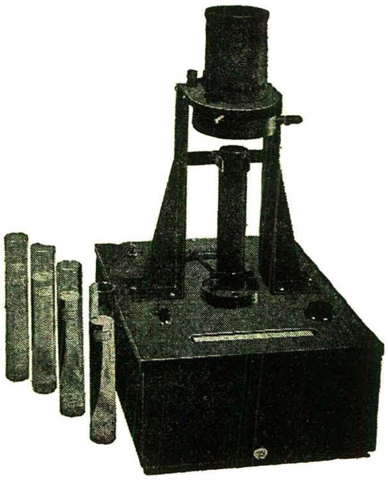

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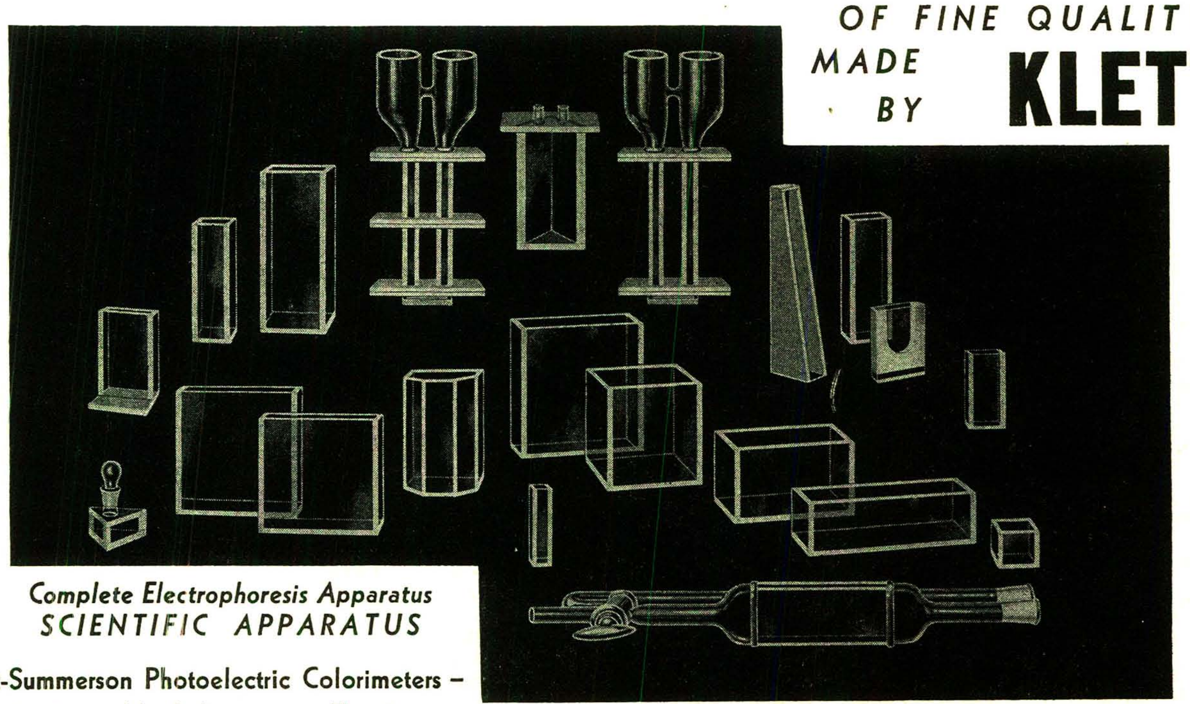

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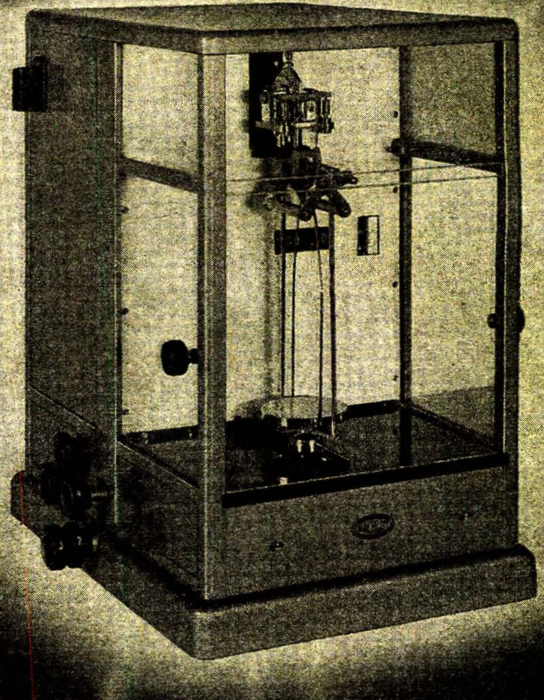

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56 Auburn Ave., N. E., Atlanta 3
Southern Scientific Co., Inc.
890 New Chattahoochee Ave. N. W.,
Atlanta

ILLINOIS
K. G. Cole Chemicals, Inc.
66 By-Pass South and B & O Railroad,
Springfield
A. Daigger & Company
159 W. Kinzie St., Chicago 10
Arthur S. LaPine & Company
6001 South Knox Ave., Chicago 29
E. H. Sargent & Co.
4647 West Foster Ave., Chicago 30
Schaar & Company
754 W. Lexington St., Chicago 7
Standard Science Supply Co.
1231-39 N. Honore St., Chicago 22
Wilkens Anderson Company
4525 West Division St., Chicago 51

INDIANA
Clark Chemical & Supply Company, Inc.
1527 Miller St., Indianapolis 7

KANSAS
Southwest Scientific Corp.
122 S. St. Francis, Wichita 2

KENTUCKY
Allied Scientific Co.
555 South First St., Louisville 2

MARYLAND
Will Corporation of Maryland
14 W. Barre St., Baltimore 1

MASSACHUSETTS
Howe & French Inc.
99 Broad St., Boston 10
E. F. Mahady Co.
851 Boylston St., Boston 16
Peakes Laboratory Supply Co., Inc.
22 Lexington St., Rear, Waltham 54

MICHIGAN
Harshaw Scientific Division
of The Harshaw Chemical Company
9240 Hubbell Ave., Detroit 28
E. H. Sargent & Co.
1959 East Jefferson, Detroit 7

MINNESOTA
Hawkins Chemical Company
3100 East Hennepin Ave.,
Minneapolis 13

MISSOURI
Aloe Scientific Division
A. S. Aloe Company
5655 Kingsbury Ave., St. Louis 12
Heil Corporation
210 S. 4th St., St. Louis 2
Kansas City Laboratory Supply Co.
307 Westport Road, Kansas City 2
Millard Heath Co.
325 Olive St., St. Louis 2

MONTANA
Northwest Chemical Laboratories, Inc.
1924 4th Ave., No., Billings

NEW JERSEY
Otto R. Greiner Company
221 High St., Newark 2
General Laboratory Supply Co.
P. O. Box 2607, Paterson
Para Laboratory Supply Company
221 N. Hermitage Ave., Trenton 8
Scientific Glass Apparatus Co., Inc.
100 Lakewood Terrace, Bloomfield

NEW YORK
Ace Scientific Supply Co., Inc.
810 Broadway, New York 3
Amend Drug & Chemical Co., Inc.
117-119 E. 24th St., New York 10
The Emil Greiner Company
20-26 N. Moore St., New York 13
Riverside Chemical Company, Inc.
871-947 River Road,
North Tonawanda
Standard Scientific Supply Corp.
34 West 4th St., New York 12
Will Corporation
P. O. Box 1050, Rochester 3
Will Corporation
(Branch of Rochester)
596 Broadway, New York 12
U. S. Scientific Supply Co.
1368 Flatbush Ave., Brooklyn

NORTH CAROLINA
Cardinal Products, Inc.
P. O. Box 1611, Durham

OHIO
Ace Chemical Company
216 Elm St., Cincinnati 2
Crowley Thompson Chemical Co.
Lederer Terminal, Foot of E. 9th St.,
Cleveland 14
The Kauffman-Lattimer Co.
(App. Dept.)
230 N. Front St., Columbus 16
Harshaw Scientific Division
of The Harshaw Chemical Co.
1945 E. 97th St., Cleveland 6
The Rupp & Bowman Co.
315 Superior St., Toledo 3

OKLAHOMA
Refinery Supply Co.
621 E. 4th St., Tulsa 3

PENNSYLVANIA
Edward P. Dolbey & Co.
P. O. Box 7316, Philadelphia 1
Scientific Equipment Company
3527 Lancaster Ave., Philadelphia 4
Arthur H. Thomas Company
W. Washington Square, Philadelphia 5

TENNESSEE
Kay Scientific Division of
Kay Surgical, Inc. Laboratory
Supply Department
1144 Madison Ave., Memphis 1
Nashville Surgical Supply Co.
401 Church St., Nashville 3
Technical Products Company
19 N. Dunlap St., Memphis

TEXAS
E. H. Sargent & Co.
5915 Peeler St., Dallas 10
Refinery Supply Co.
2215 McKinney, P. O. Box 20509,
Houston, Texas

UTAH
Denver Fire Clay Company
225 West South Tem
Salt Lake City 1

WASHINGTON
Scientific Supplies C
122 Jackson St., Se

WEST VIRGINIA
B. Preiser Company, Inc.
416 W. Washington St., Charleston 2

WISCONSIN
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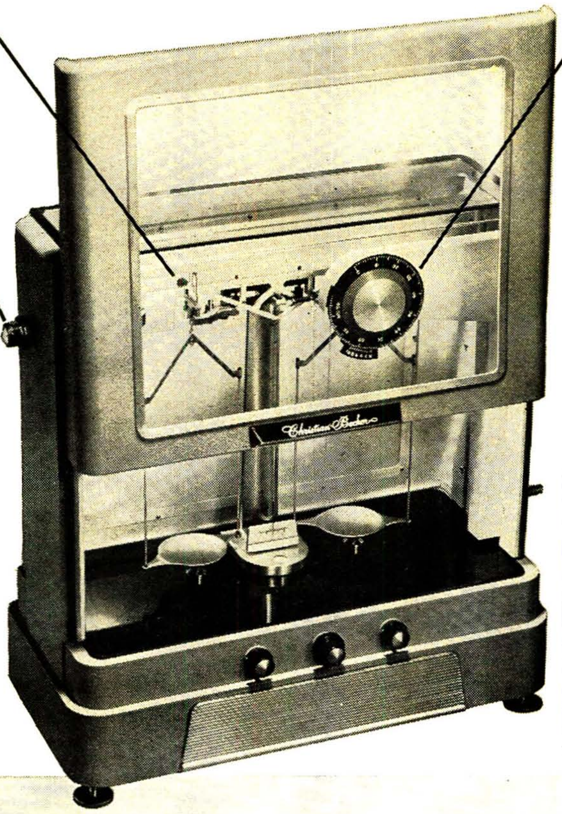

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