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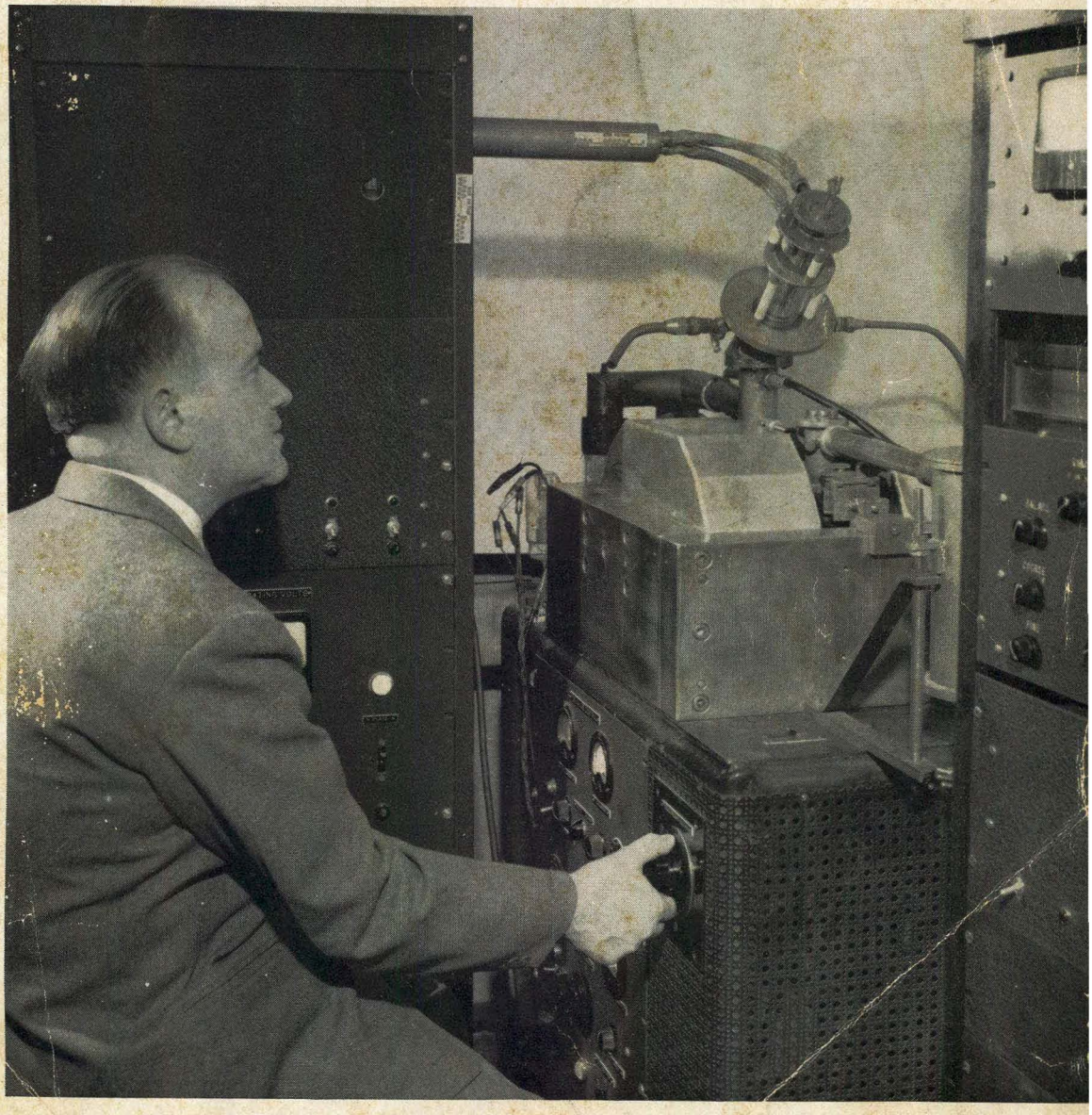
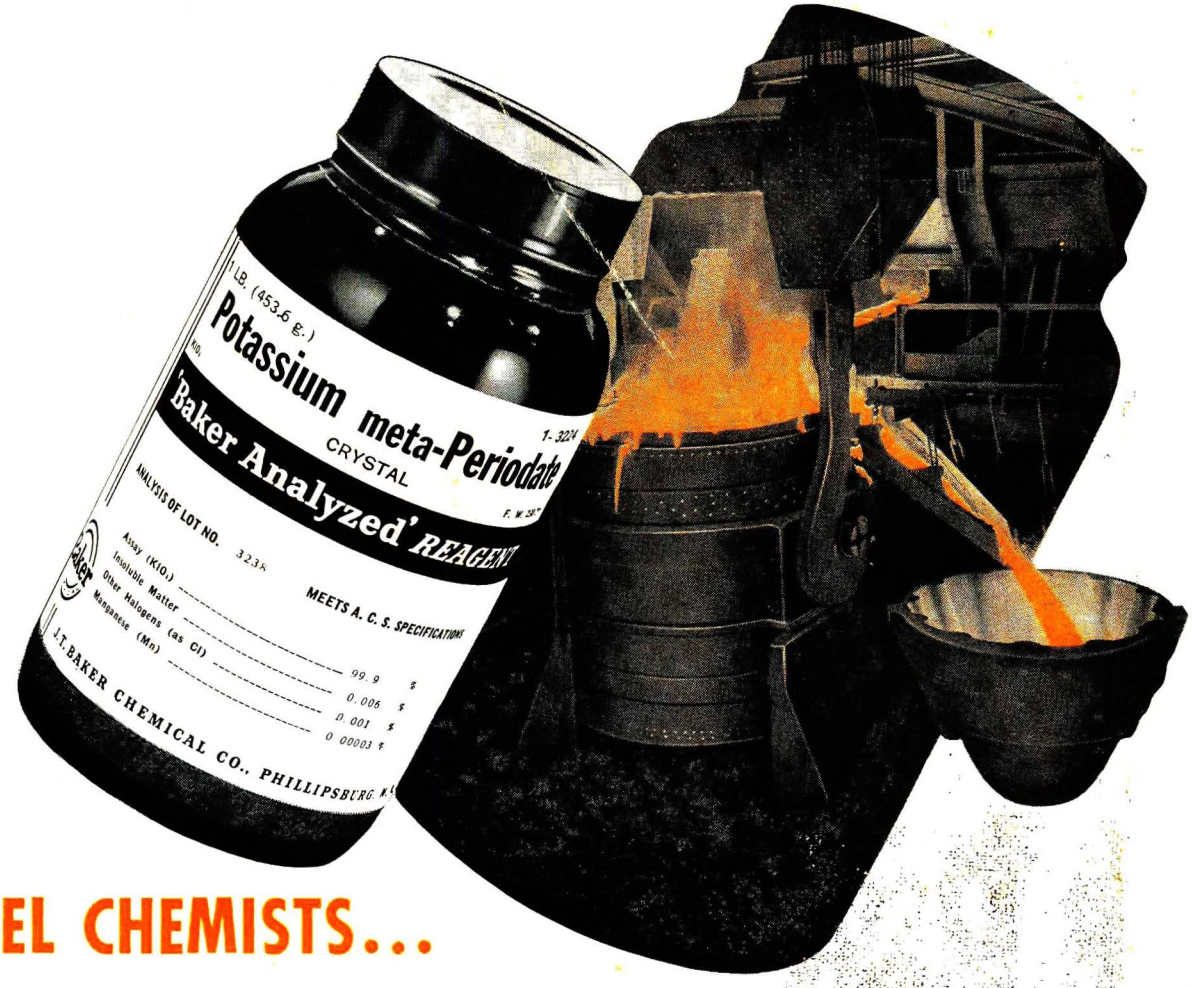
ANALYTICAL CHEMISTRY



New technique makes possible wide application of mass spectrometer in routine, rapid analysis of solids



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This Month's Cover. The mass spectrometer has been applied with great success to the analysis of gases and vapors, but it has not been used generally for solids for lack of a suitable technique. Recently, however, J. A. Hipple (shown in photo) and his associates at the National Bureau of Standards have developed a method whereby a spark source can be used in an instrument employing electrical recording. First described in detail in ANALYTICAL CHEMISTRY (23, 438, 1951), the procedure is said to yield highly accurate, easily interpreted results with much greater speed than chemical methods. The NBS method stems from the basic work of A. J. Dempster and his associates at the University of Chicago.

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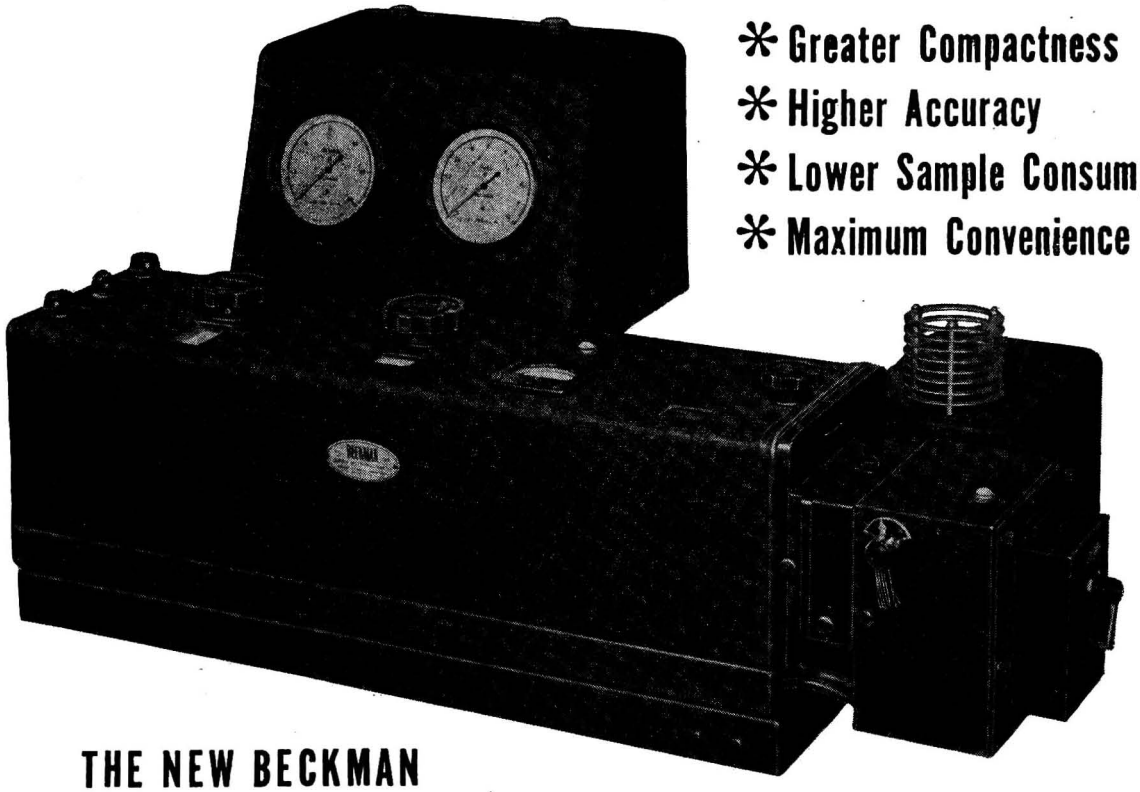

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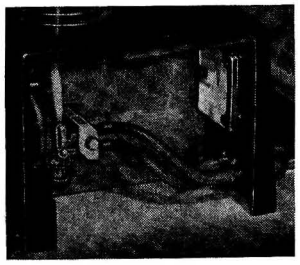

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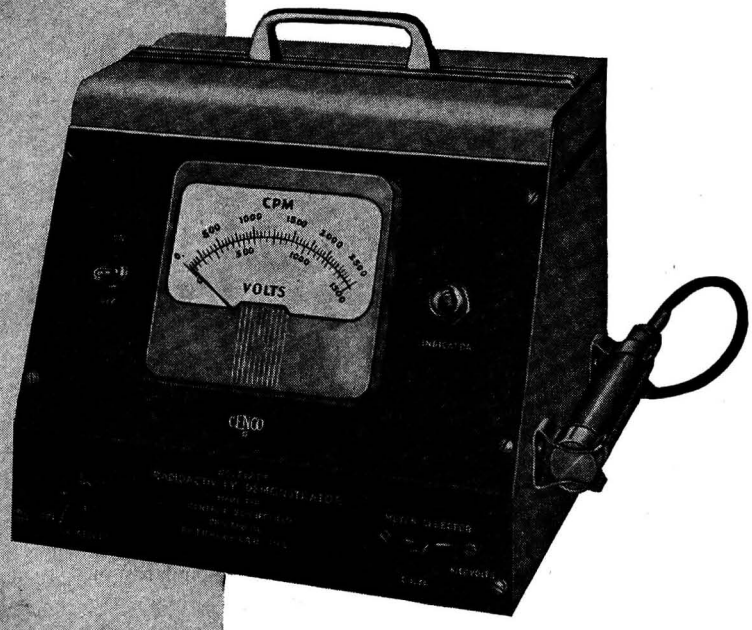

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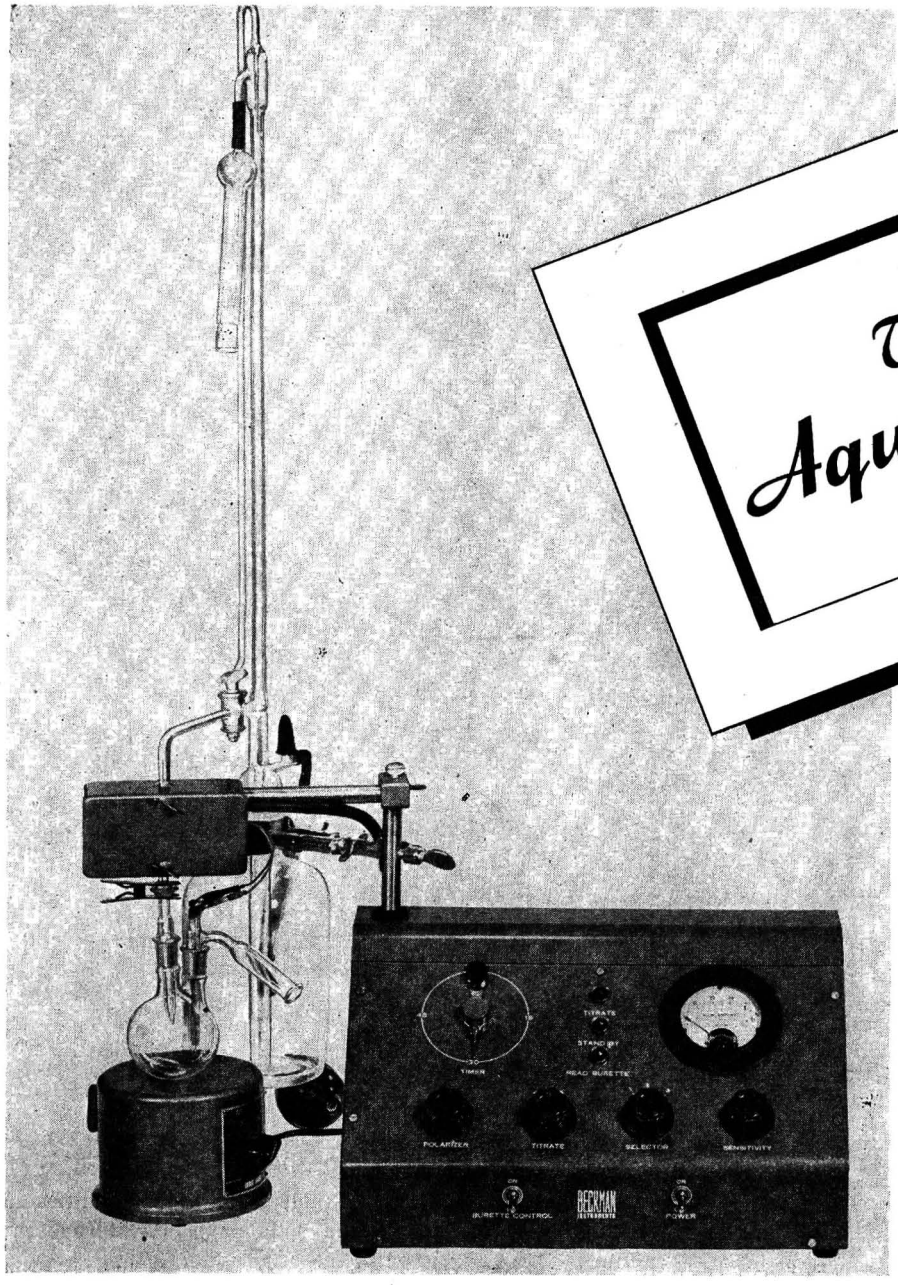

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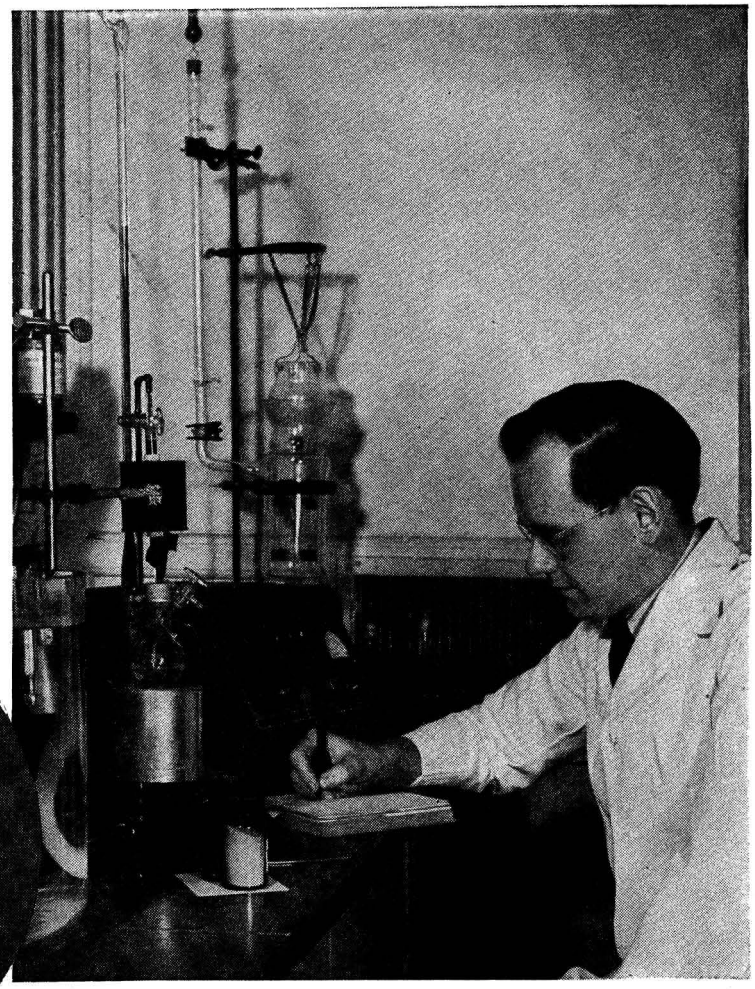

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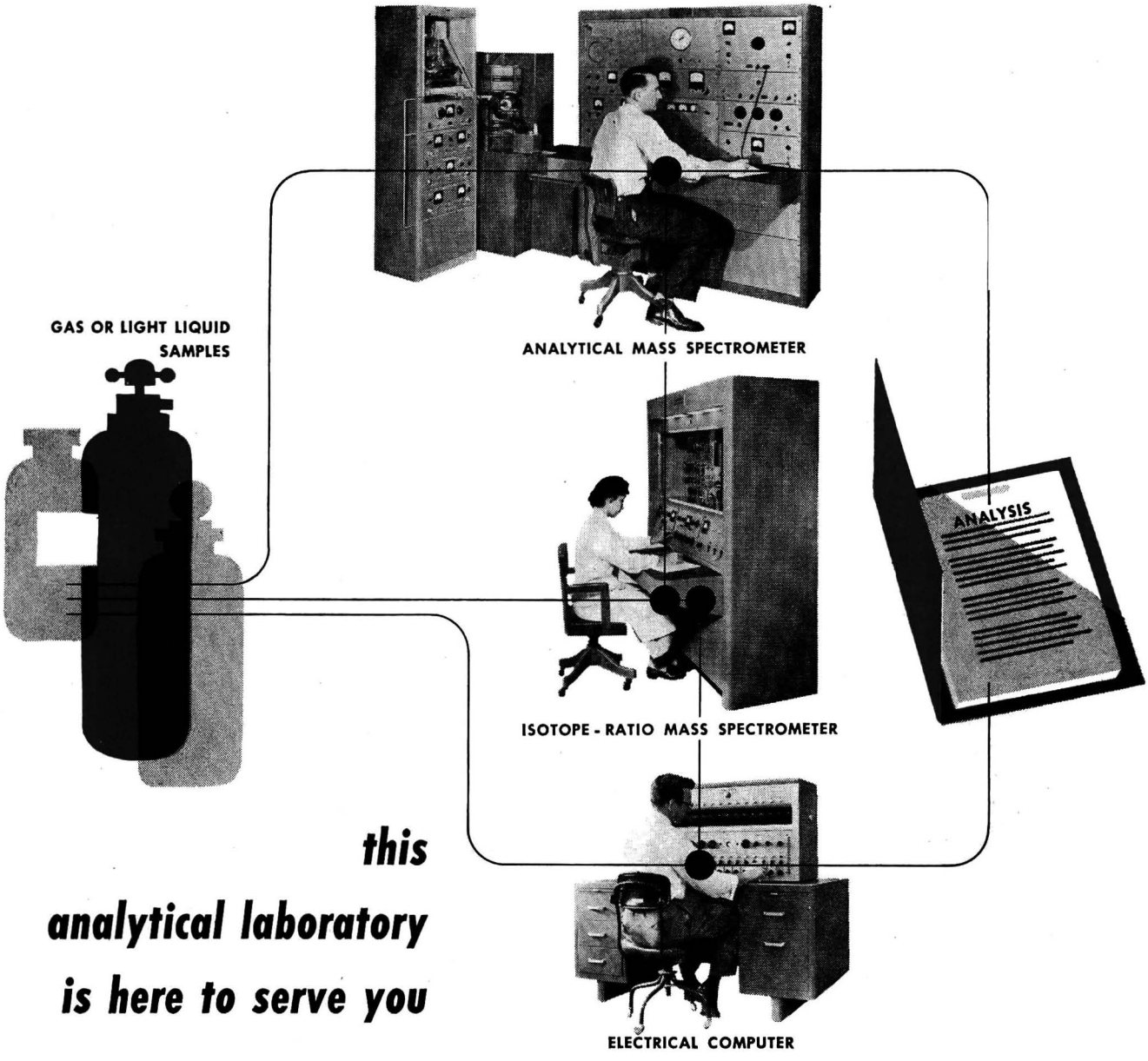

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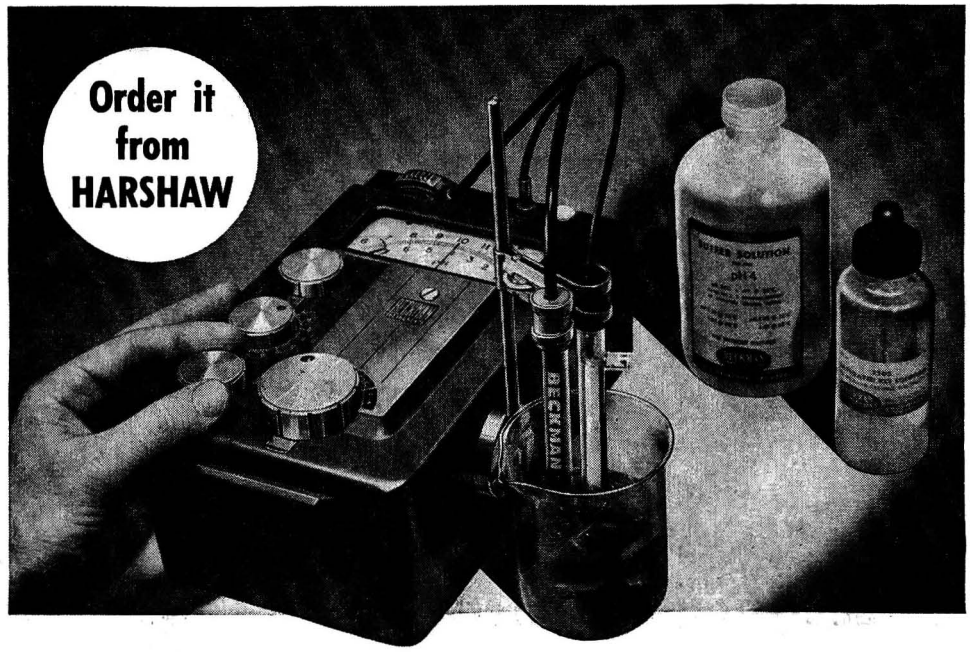

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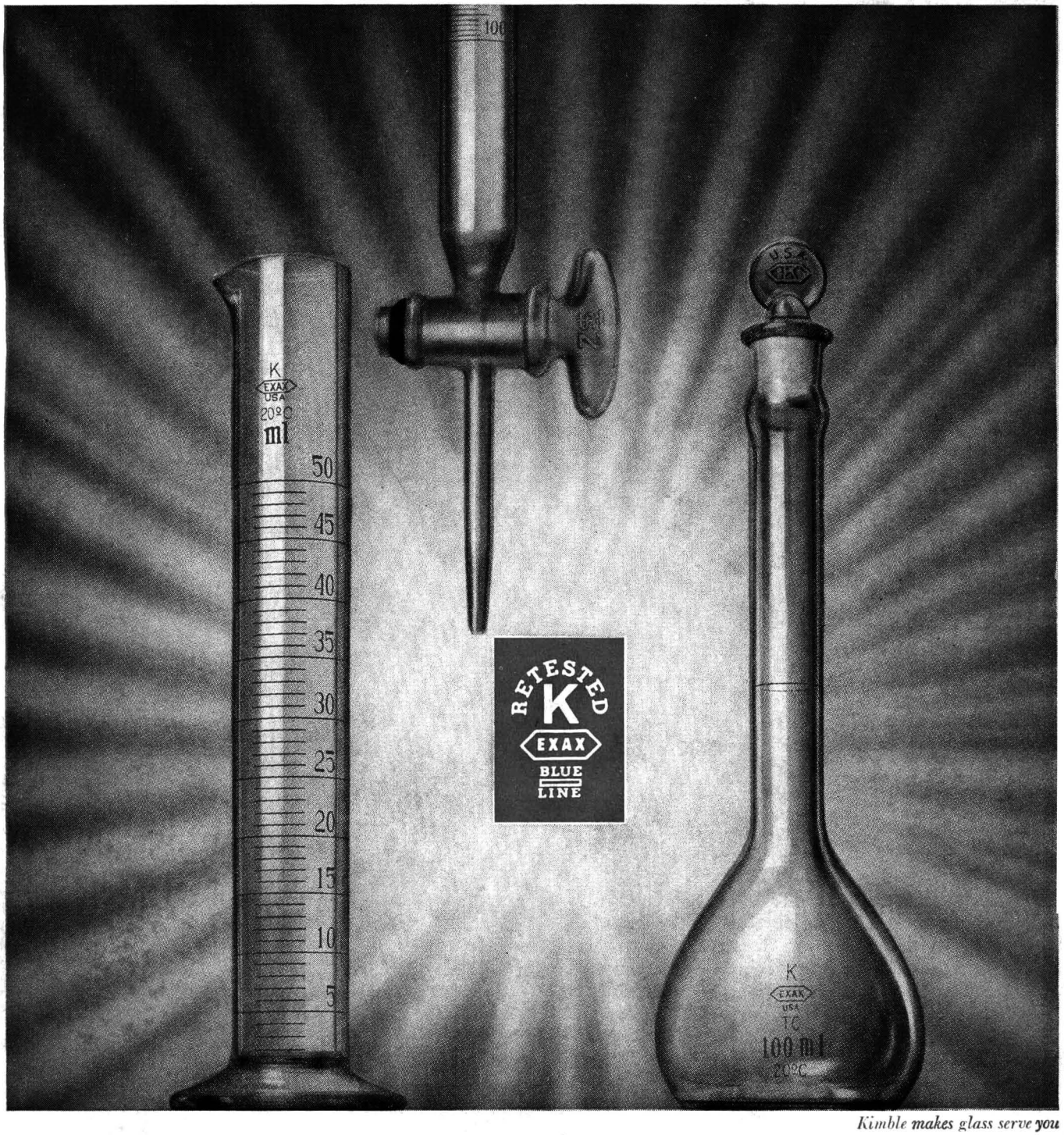

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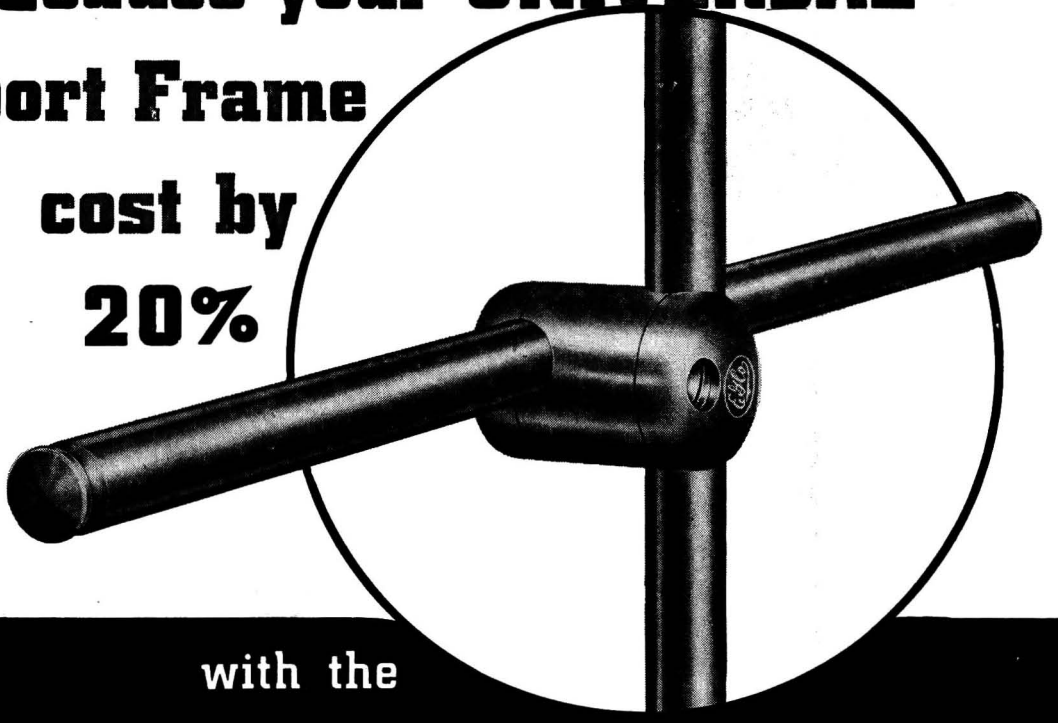

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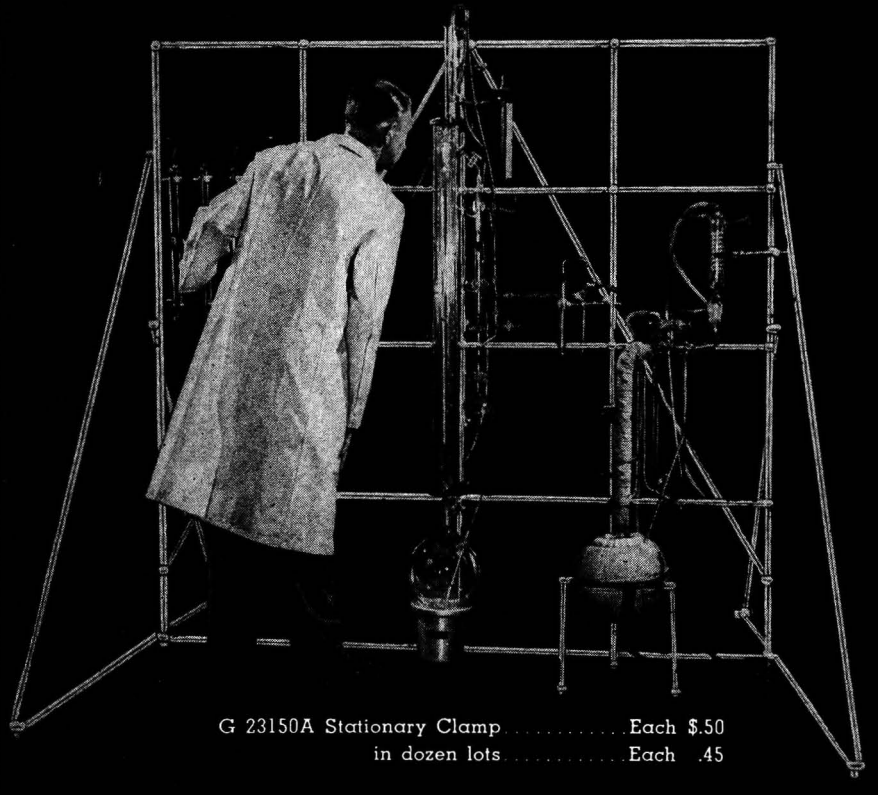

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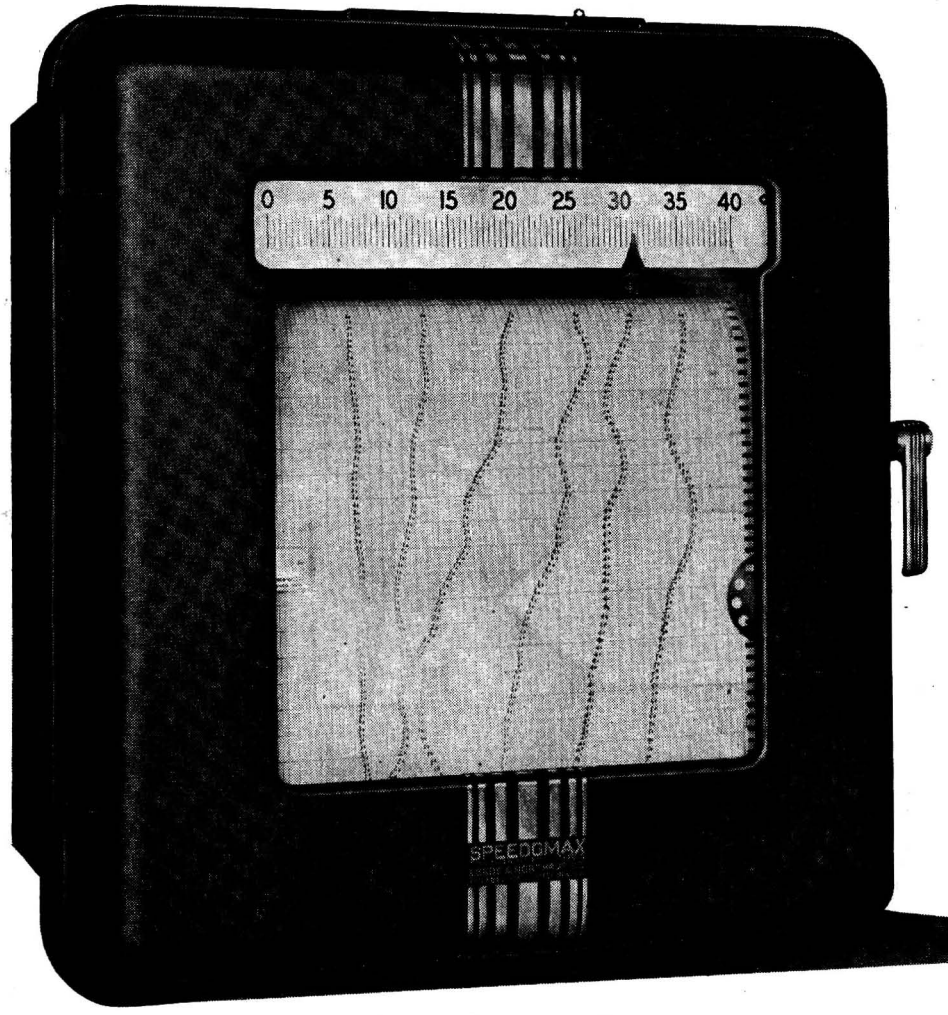

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Multiple-point Speedomax recorder at left is a familiar sight in scientific laboratories throughout the world. While the 6 new instruments described below all *appear to be* practically identical, each *is different* from the others.

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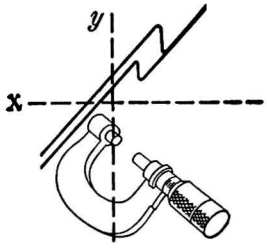
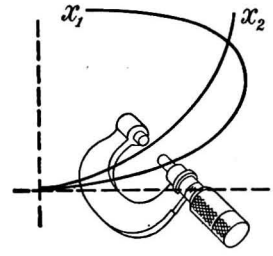


SPEEDOMAX X-Y RECORDER

Automatically plots the relationship between any two variables which can be converted to d.c. signals. Both pen and chart motion are reversible. Instrument records vacuum tube characteristics, hysteresis loops, stress-strain, temperature-elongation, differential thermal analysis curves . . . Applications are as broad as a researcher's imagination. *Write for Folder EM9-420(2).*

SPEEDOMAX ADJUSTABLE RANGE-ZERO RECORDER

Automatically plots voltage representing force, weight, temperature, temperature-difference, speed . . . or any other condition. Suppressing ZERO pushes *non-significant mv* off scale. Adjusting RANGE spreads few significant mv right across chart. Range *continuously* adjustable from —0.1 to +1 mv . . . up to —2 to +20 mv; zero suppression, from —50 to +50 mv. Folder ND46(2).



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AS the tempo and complexity of today's research and engineering activities accelerate, more and more investigators are stepping up efficiency through use of time-saving Speedomax recorders. Tireless automatic assistants, these electronic servants are taking over the chores of routine computation . . . eliminating tedious manual plotting of data.

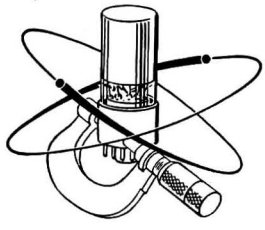
Especially timely are these 6 new Speedomax recorders developed specifically for laboratory use. While each is a *specialist*, it is also designed for a diversity of applications.

Common denominators for all six are traditional Speedomax precision and high-speed response. Recording pens can whip across the 9⅞" chart in as little as *1 second*, if the application demands, though speeds of 2 and 3 seconds full scale are also available. Balancing is velocity-damped to take advantage of this high speed.

Alert to the most minute variation in "X," the sensitive electronic balancing system is the perfect complement for the instrument's accurate null-balance measuring circuit. Thorough filtering, shielding and guarding screen out transients . . . permit use of Speedomax in the presence of severe stray fields.

Net result: the investigator can follow complex, fast-changing variables with ease and confidence . . . knowing that the record on his Speedomax is faithfully following the actual function being measured.

can solve your data-logging problems . . .



SPEEDOMAX PHOTOMULTIPLIER TUBE RECORDER

Automatically plots accurate record of light intensity or other low level radiation. Can be direct-connected to photo-multiplier tubes . . . eliminating separate preamplifier. Available by switch are four ranges: 0.02, 0.06, 0.2, and 0.6 μs. Dark current or noise of photo-multiplier tube is readily offset by built-in manual compensator. *Write for DS-240-70-EM9(1) to (3).*

SPEEDOMAX POWER LEVEL RECORDER

Automatically plots radiation patterns of antennas and hydrophones . . . frequency characteristics of filters, amplifiers, loudspeakers, etc. Applies accurate "insertion loss" principle of measurement. Recorder can be supplied with full scale reading of 20, 30, 40, 50, or 60 db, referred to a base level of as little as 0.02 microwatt. *Write for Folder ND46-51(1).*

SPEEDOMAX PRECISION THERMOMETER RECORDER

Automatically plots temperature curves for calorimetry, freezing and boiling points . . . reads resistance of platinum thermometer to five significant figures. An "automatic Mueller Bridge," it covers the entire range from —260 to +500 C with precision of ±0.01 C. Automatic range-changing mechanism expands chart width 100 times. *Write for Folder ND46-33-240(1).*

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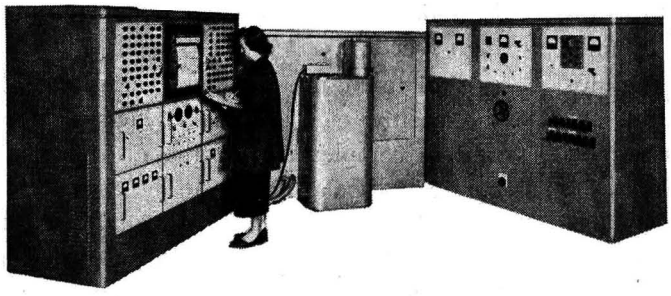

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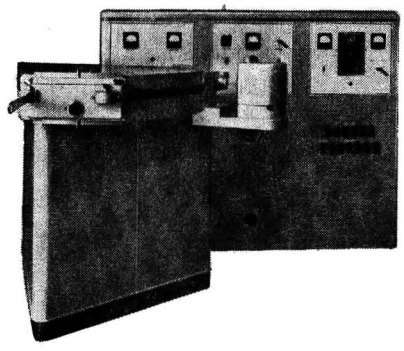

Extremely compact and versatile. Uniform dispersion over entire spectrum range. Original grating gives marked superiority in detecting elements in low concentrations. Paschen mounting for camera covers extensive spectrum range. Excitation stand handles flat and pin samples for both quantitative and qualitative analyses.

Source units are available in types to meet all testing requirements.

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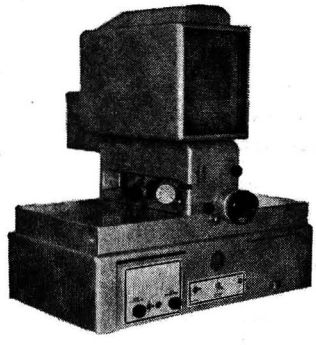

This instrument is manufactured to the highest ARL standards, permitting the most accurate qualitative and quantitative analyses, based upon spectrum line positions and densities. It is easy to adjust and the image is located in a non-fatiguing viewing position. As many as 6 lines per minute can be easily read.

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the analyst's column

THE Committee on Infrared Absorption Spectra about which we wrote in October, has issued the following interim report:

About the first of September 1951, an announcement of the formation of this committee, its objectives and personnel was sent to about 1200 workers in the field of infrared spectroscopy. This figure represents about 370 organizations that sent representatives to the Columbus symposium. Included with the announcement was a questionnaire for use by the committee in estimating the number of sets of punch cards to be printed and the extent of the punching to be put on the cards prior to distribution. Eighty-four letters and questionnaires were returned (23% of the possible 370), 71 of which expressed definite interest. On the basis of these returns, the cost of compound cards is estimated to be of the order of 10 cents each and bibliography cards of the order of 5 cents each.

The 71 quessionnaires are tabulated as follows:

Interested in compound cards	67
At 25 cents per card 21	
At 15 cents per card 30	
At 10 cents per card 12	
No price indicated 4	
Extra sets	4
Total number of sets of compound cards	71
Interested in bibliography cards	
At 15 cents per card 14	
At 10 cents per card 23	
At 5 cents per card 18	
No price indicated 3	
Laboratories which can contribute spectra	48
Estimated number of spectra which will be available the first year	2900
Number of laboratories wishing compound cards completely punched	51
Number of laboratories wishing compound cards punched except for wave length	10
Number of laboratories wishing compound cards completely unpunched	6

There is a probability that there will be a fair amount of duplication of the spectra from the 48 laboratories, so that the 2900 spectra available the first year will yield somewhat fewer than that number of spectra for publication. There are available, however, more spectra than can probably be processed during the first year's activity.

The responding laboratories may be grouped into the following types:

University laboratories, %	20
Government laboratories (50% military), %	23
Industrial laboratories, %	57

(*Continued on page 19 A*)

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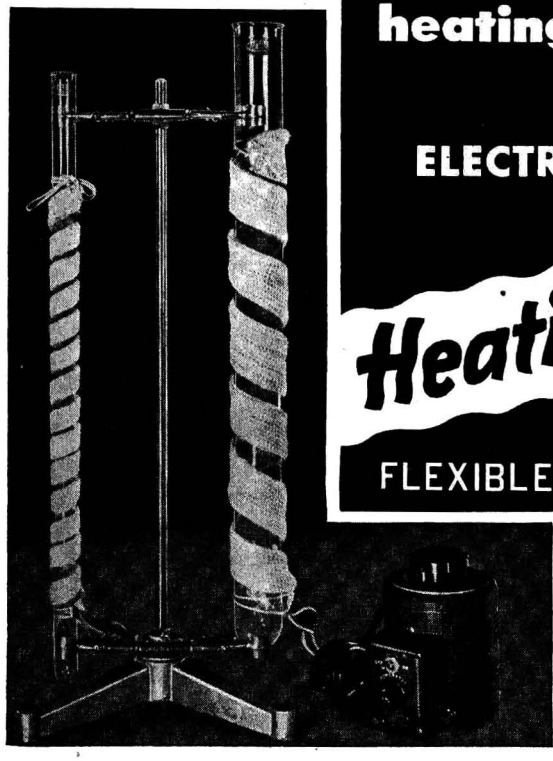

FLEXIBLE CONSTRUCTION ALLOWS FLEXIBILITY IN USE

THIS INSULATED, flexible tape—made of sturdy, temperature-resistant glass fiber yarn—is the answer to a myriad of heating problems in the laboratory. For the flexible, elastic qualities of this tape enable even heating of any vessel, tube, pipe or other object regardless of shape. Simply wind or wrap Electrothermal tape around the object to be heated and turn on the "juice." Any suitable control device such as a variable auto-transformer, rheostat or other energy regulator may be used.

But when used in conjunction with the all-purpose Powerstat (pictured with the tape set-up above), the operator may select the voltage that will provide the degree of heat desired by simply turning the voltage regulator dial on top of the unit. Voltages between 0 and 135 may be obtained. And once the desired setting is made, constant heat is assured.

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"	48″ x 2½″	1.5	14.90	18.75
"	60″ x 3″	2.3	20.15	26.45
"	72″ x 3½″	2.6	22.95	29.40

#32-072 POWERSTAT—Variable Transformer—1 KVA capacity, Output Voltage Range 0 to 135v.....$23.00

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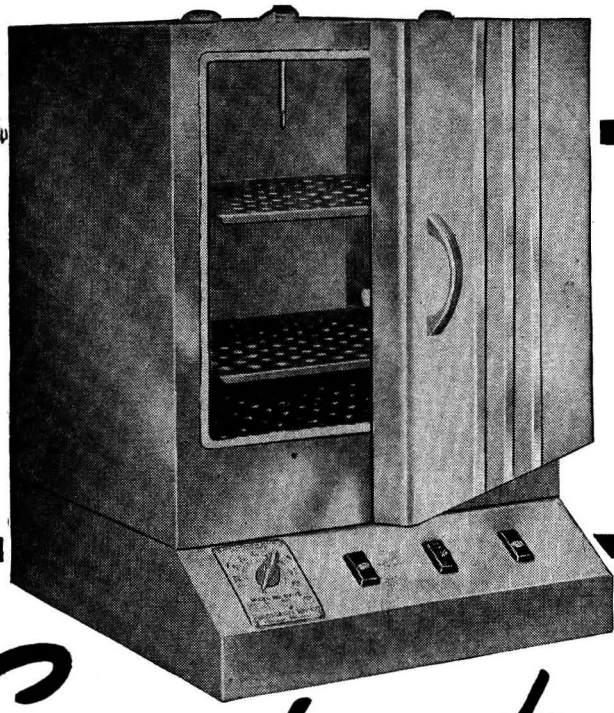

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CONSTRUCTION—Outside housing, door and base are made of beautiful shining No. 4 finish Stainless Steel (Type 302, 18-8). The inside working chamber is made of No. 2 finish Stainless Steel (Type 302, 18-8). Two adjustable shelves of electro-polished Stainless Steel Wire.

INSULATION—All six sides insulated with 1½" layer of fiber glass wool in Models SN-4440 and SN-4400, and 2½" layer in Models SN-4500 and SN-4480. Keeps heat loss at a minimum and outer surfaces cool even after prolonged use.

VENTILATION—Intake ports at bottom allow fresh air to enter. Double exhaust ports at top, with Stainless Steel slides, control exhaust fumes.

HEAT CONTROL—Sensitive, powerful, automatic hydraulic electric thermostat conveniently mounted on front allows easy setting of temperatures. Graduated for Fahrenheit and Centigrade readings; response sensitivity ±½° C.

HEATING ELEMENT—Heavy Nichrome V resistance wire, spread over entire base of inside chamber. Positive temperature uniformity assured.

DOOR—Fully insulated, hung on a continuous hinge and fitted with a fool-proof latch designed to insure safety. Exclusive dovetail design gives positive seal.

PILOT LIGHTS—Red neon light denotes unit operation, green neon light for thermostat operation.

MODEL SN-4440—A most popular oven, 12" x 12" x 12" inside. Temperatures to 232 deg. C. (100 to 450 deg. F. range). Two adjustable Stainless Steel shelves, 6-foot cord and plug. For 110 volt, 60 cycle, single phase A.C. current. 800 watts..... **$117.50**

MODEL SN-4460—Same as SN-4440, but 110 volt D. C..... **$127.50**

MODEL SN-4400—New, small size—only 8" x 8" x 8" inside. Temperatures to 204 deg. C. (100 to 400 deg. F. range). One Stainless Steel shelf, thermometer, 6-foot cord and plug. For 110 volt, 60 cycle, single phase A. C. current. 500 watts..... **$75.00**

MODEL SN-4420—Same as SN-4400, but 110 volts, D. C..... **$85.00**

MODEL SN-4480—A DeLuxe, large size, high temperature oven, 18⅞" x 17¾" x 14¾" high inside. Temperatures up to 288 deg. C. (100 to 550 deg. F. range). Two adjustable Stainless Steel shelves, thermometer, terminal block for electrical connections. For 110 volt, 60 cycle, single phase A. C. current. 1750 watts..... **$225.00**

MODEL SN-4490—Same as SN-4480, but for 220 volt, 60 cycle, single phase, A. C. current..... **$235.00**

MODEL SN-4500—Similar to SN-4480. Stainless Steel interior but baked enamel exterior, and aluminum coated shelves. For 110 volt, 60 cycle, single phase A. C. current. 1750 watts..... **$175.00**

MODEL SN-4510—Same as SN-4500, but for 220 volt, 60 cycle, single phase A. C. current..... **$185.00**

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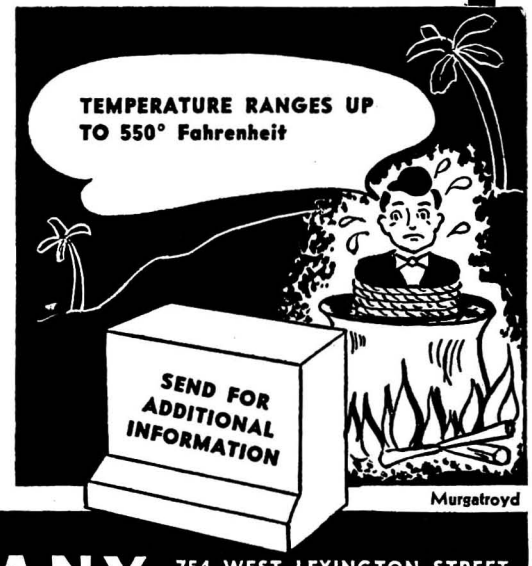

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THE ANALYST'S COLUMN

Besides the promises of spectra and aid in the abstracting program, government laboratories have supplied an estimated $30,000 to $40,000 toward getting the project started. None of this money can be contributed toward the working fund (contributions are prohibited by law). However, the bibliography and the index by compounds can be contributed. The index by compounds covers about 2600 compounds which have been obtained as a result of studying in the original about 18% of the bibliography. This study will be continued until the bibliography has been covered.

Investigation of offset printing processes has resulted in the discovery of two new multilith masters (one of which is not yet on the market), capable of reproducing 390-line half-tone screens. By the use of these, there should result printed spectra of sufficient detail to satisfy the most critical user.

In order to print and sell spectra on punch cards, the committee has had to solicit working funds. Of the 39 industrial laboratories responding to the questionnaire, thirteen have supported the project to the (total) extent of $6000. They are:

Abbott Laboratories, Chicago, Ill.
Allied Chemical and Dye Corp., Barrett Division, New York, N. Y.
Allied Chemical and Dye Corp., National Aniline Division, Buffalo, N. Y.
Arthur D. Little, Inc., Cambridge, Mass.
Eastman Kodak Co., Rochester, N. Y.
Eli Lilly and Co., Indianapolis, Ind.
General Electric Co., Schenectady, N. Y.
Hercules Powder Co., Wilmington, Del.
Merck and Co., Inc., Rahway, N. J.
Minnesota Mining and Manufacturing Co., St. Paul, Minn.
Procter and Gamble Co., Cincinnati, Ohio
Standard Oil Co. (Indiana), Chicago, Ill.
Stanolind Oil and Gas Co., Tulsa, Okla.

The committee thanks these organizations for their support.

E. Carroll Creitz, secretary of the committee, which is operating in collaboration with the National Bureau of Standards, points out that while progress is satisfactory to date, it is hoped that more contributions will be forthcoming to help carry on the work of this project even more effectively.

Associate Editor

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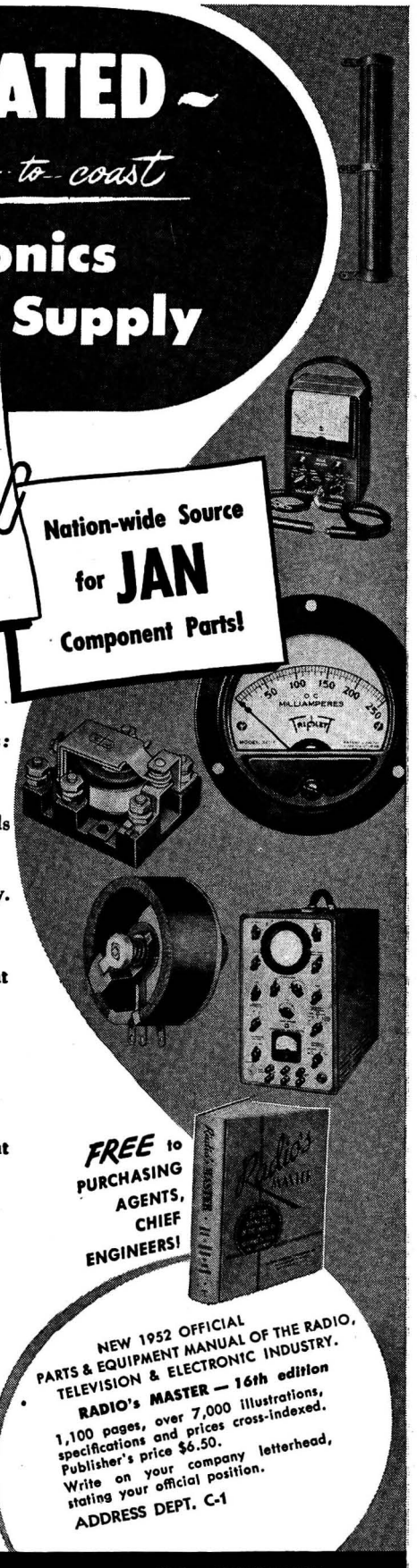

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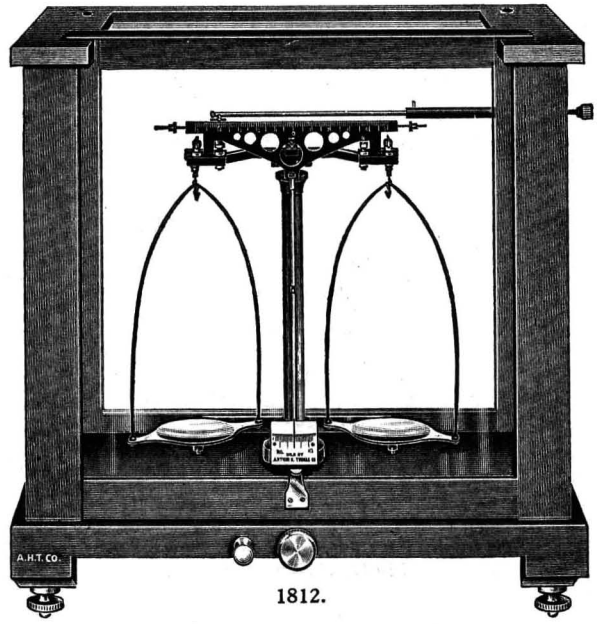

1812.

ANALYTICAL BALANCE, A.H.T. Co. Model H-1. An improved execution of a time-tested, simplified design, without drawer in base, intended for use in industrial or educational laboratories for quantitative analysis. Especial attention has been given to the design of the beam, beam support, stirrups and stirrup rests, so that erecting and cleaning can be accomplished quickly and with minimum danger of damage to the delicate parts such as agate knife edges, etc. The rider carrier is mounted on a slotted rod of Duralumin and will pick up and accurately adjust the rider without striking the beam.

Sensitivity—0.1 milligram with full load. Adjusted so that the change of weight of 1 mg on the pan deflects the pointer on the scale at least 2½ divisions.

Capacity—200 grams in each pan.

Case—Of mahogany, with counterpoised front door, circular level and leveling screws, but without drawer in base. Overall dimensions, 16½ inches wide × 16 inches high × 9½ inches deep.

Central Pillar—Of Duralumin, oxidized black, ⅝-inch diameter.

Beam—Of hardened aluminum, 6 inches long, with oxidized black finish. Graduated in white on both sides of central knife edge from 0 to 5 mg in 1/10 mg divisions, using a 5 mg rider.

Rider Carrier—Mounted on a slotted rod of Duralumin; will pick up and accurately adjust rider without striking the beam.

Knife Edges and Planes—Of agate throughout.

Release and Arrest—The beam and hangers are released by a single action device making the contact of the central knife edge simultaneous with the contact of the end knife edges and bearings. The construction of the arresting device is simple and rugged, engaging and supporting the beam and hangers free of any contact with the knife edges and bearings, thus preventing any possible damage while loading and unloading the pan.

Pointer Scale—Of ivory, recessed so that the end of the pointer moves in the offset in the same vertical plane as the division on the scale, thus avoiding errors of parallax.

Pan Arrest—Self-locking, adjustable push-button type.

Pans—Of polished Duralumin, 2½ inches diameter.

Arches—Of polished Duralumin, height 7½ inches, spread 4 inches.

Riders—Each balance is furnished with two 5-mg aluminum riders.

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ANALYTICAL CHEMISTRY

Walter J. Murphy, Editor

The Merck Fellowship Renewed

In September of 1948, the Board of Directors of the American Chemical Society accepted a proposal by Merck & Co., Inc., that the Society administer a graduate fellowship in analytical chemistry financed by the company. Merck & Co. agreed to support the fellowship for three successive years at an annual stipend of $2500. We are very happy to report the Merck Board of Directors has decided to renew the arrangement with the Society for another three years.

We may be pardoned if we derive considerable personal satisfaction from the initial success of the Merck Graduate Fellowship in Analytical Chemistry.

In March 1947 an editorial in Analytical Chemistry proposed a four-point program for improving the profession of analytical chemistry. One of the suggestions was the establishment of a number of postgraduate fellowships. This suggestion was brought to the attention of George Merck by Randolph T. Major and Beverly L. Clarke. Within a few months Merck & Co. directors forwarded a concrete proposal to the Society which was quickly accepted.

No strings are attached to the Merck Graduate Fellowship in Analytical Chemistry. A fellow is eligible to have his fellowship renewed twice, but no person may hold the fellowship for longer than a total of three years. Each applicant or nominee must establish to the satisfaction of the ACS award committee that he is acceptable for graduate work in analytical chemistry at a specified, ACS-approved institution in the United States or Canada, and a proposed research and study outline must be submitted to the award committee.

Once again our heartiest congratulations and deep-felt thanks to the directors of Merck. When we editorialized on the fellowship in 1948, we stated:

> Here is a very practical way of demonstrating that private enterprise in the chemical field has a deep and lasting interest in the progress of the chemical profession. Here is an opportunity for industry to assist the youth of America to gain professional training in one of the most challenging professions, as well as to help to provide the scientific manpower which it will surely need if the present rate of progress is to be maintained and accelerated as it should be in the future.

These words were written in October of 1948. They were pertinent then—they are much more pertinent today.

The action of Merck & Co., Inc., in renewing its offer for another three years can be construed as an endorsement of the manner in which this fellowship has been administered by the Society.

The Society does have well developed methods of procedure for administering fellowships at the predoctoral and postdoctoral levels. There is great need for fellowships in every branch of chemistry and chemical engineering. We hope many other companies in the chemical and chemical process fields, companies engaged in the design and marketing of heavy process equipment, and companies making and distributing scientific apparatus will consider seriously the establishment of one or more fellowships to be administered by the American Chemical Society. The experience of Merck & Co. is an ample guarantee to donors that such fellowships will be handled in a highly satisfactory manner.

Random Thoughts of the Editor

More than three years ago we introduced a new department, "Communications to the Editor," to be devoted exclusively to scientific matters. We must admit we are disappointed with the paucity of communications. Perhaps we have not publicized the department frequently enough.

We have just received as a member of the Division of Analytical Chemistry a unique mailing piece from Beverly L. Clarke, the new chairman of the division, and William G. Batt of the Biochemical Research Foundation, Newark, Del., our hard-working secretary and treasurer.

On one portion of this unique mailing piece is a message from our new chairman—the rest is a handy envelope for mailing your one dollar division dues for 1952. Your continued interest and financial support will mean much for the profession of analytical chemistry now and in future years.

In the year just passed, Analytical Chemistry published 2026 editorial pages. The Board of Directors has authorized an additional 114 pages for 1952, an increase of 5.5%. In 1950 we published 1614 pages and in 1944 782 pages. Our duties multiply rapidly, but we are very happy, for this growth indicates (1) the sustained expansion of the science of analytical chemistry, and (2) that the journal continues to meet the publication needs of analysts in every part of the world.

4th Annual

Review of Analytical Chemistry

FOR the fourth 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 the February issue nine articles will review 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.*

THERE seems little doubt today about the importance in testing and analytical laboratories of measurements of the absorption of radiant energy in the visible region of the spectrum. Scientists and technologists work with materials in terms of what is present and how much of each constituent there is, information now often easily obtained in this way. Also, multitudes of people everywhere are concerned with describing and specifying the color of objects.

As long as better methods and means of operation are found, or improvements are made in old ones, there will be advances to report. Included also are new and different applications to materials. The past year has brought no diminution in the number of such items published. The papers cited from this journal may be taken as an indication of the popularity of the subject.

The outline used by the writer in previous reviews has been substantially retained. Again completeness of coverage has not been attempted, as representative selections seem adequate to show the trend of developments. Such selection is especially to be noted in the sections on color formation in organic systems, and on the analytical application of color-forming reactions.

CHEMISTRY

To the reviewer the problems of chemical transformations are predominant when one tries to devise analytical methods for many multicomponent systems. At least his own graduate students have the great majority of their difficulties at this point. One must build procedures around the transformations possible for the given constituent(s). Once a constituent is in suitable form, and interferences are absent or provided for, measurement is generally easy with modern equipment. Apparently, the problem is general, judging by the host of papers bearing upon finding better colored forms for measurement, easier processes to obtain them, and improved understanding and control of the processes.

Nature of Absorbing Systems. The question of the identity and nature of absorbing species in a colored solution remains intriguing in many cases. Papers dealing with the subject may be subdivided roughly into (1) those of a general nature, with a rather broad consideration of methods and results, and (2) those reporting on specific systems.

A book by Charlot and Gauguin (*56*) summarizes the general methods found useful for determining species and for analyzing reactions in solution. Included is the use of spectrophotometric methods for the qualitative determination of absorbing entities.

Turning to the papers of a general nature, Kiss (*145*) summarizes the results of two decades of investigations on various systems especially inner-complex compounds. In another paper (*146*) he reports the absorption spectra for hydrated ions of many elements. In discussing the general nature of internal complexes Montequi (*191*) cites 61 references.

Babko (*18*) discusses the items regarding complexes susceptible to study by physicochemical analysis. Harvey and Manning (*111*) propose a new spectrophotometric method and a modified molar-ratio method for establishing formulas of colored complexes in solution. Fronaeus (*93*) claims a new method for investigating complex equilibria and determining complexity constants. Sone (*251*) notes a new regularity of the absorption bands of certain complexes of cobalt(III), chromium(III), and nickel(II).

Jonckers (*132*) cites 106 references in summarizing the characteristic effects of atomic groups in modifying the reactive properties of known reagents. A theoretical paper (*43*), dealing with the relation between absorption intensity and molecular dimensions, compares observed and calculated absorbance indexes. Kravets *et al.* (*152*) use Ostwald's dilution law in dealing with deviations from Beer's law attributed to the formation of several components.

The reports on specific systems are a rather miscellaneous lot. The nature of the cobalt-thiocyanate complex rates three papers, two for aqueous solutions (*167*, *278*) and one for organic solvents (*140*). Other cobalt(II) complexes studied include the halides in propyl (*27*) and in butyl (*28*) alcohol, the chloride in various solvents (*139*), and the nitrate in organic solvents (*138*).

The concept of an "interaction" complex has been proposed by McConnell and Davidson (*171*, *173*) in a study of the optical interaction between chloro complexes of copper(I) and copper(II) in solution. The method was applied to iron(II and III) systems (*172*), tin(II and IV) systems (*47*), and hexacyanatoferrate systems (*127*).

Typical of papers on organometallic complexes are the following: 2,2′-bipyridine with iron(II) (*154*, *155*); pyridine, 1,10-phenanthroline, and 8-quinolinol with silver (*250*); several amino

acids with various metals (*178*); pyramidone with aluminum, chromium, and iron (*109*); citric acid with uranium (*84*); sulfosalicylic acid with iron(III) (*89*); alkannin and naphthazarin (*270*) and quinalizarin (*181*) with beryllium; several organic compounds with different metals (*156, 157*); and thenoyltrifluoroacetone with thorium (*70*).

Papers on systems of a somewhat different nature deal with iodine in acetone (*33*); cobalt(II), nickel(II), and chromium(III) in fluoboric acid (*238*); manganese(III) in hydrochloric acid (*126*); and iron(III) in the perennial thiocyanate solution (*57*).

Bergamini (*35*) studied certain interference effects on heteropoly acids containing molybdenum coordinated with arsenic, phosphorus, or silicon. The effect in the case of molybdosilicic acid, especially, may be made the basis of a methd for determining fluorine.

Doty and Steiner (*73*) discuss the possibilities of spectrophotometry for studying solute species in colloidal solutions.

Study of Old Methods. Without spending an undue amount of time in checking details, the reviewer has been unable to decide with certainty whether some methods are really old or new. He assumes that errors in placement here are not crucial.

Examples of using organic reagents for inorganic constituents follow: ruthenium with thiourea (*15*) and with dithiodioxamide (*16*); copper with cuproine (*123*), with salicylic acid (*103*), and with sodium diethyldithiocarbamate in the presence of ethylenediaminetetraacetic acid (*241*); magnesium with 8-quinolinol (plus diazotized sulfanilic acid) (*223*); boron with morin (*130*); aluminum with alizarine-3-sulfonate (*214*); nickel in small amounts (*161*) and large amounts (*29*) with dimethylglyoxime, and in small amounts with α-furildioxime (*97*); at least a dozen constituents with pyramidone (*94*); cerium(IV) with benzidine (*193*); thallium(III) with benzidine blue (*153*); gold with *o*-tolidine (*240*); cobalt with combined benzidine and dimethylglyoxime (*166, 224*); chromate with diphenylcarbazide (*21*); selenium (*164*), iodide (*163*), and various oxidants (*162*) with linear starch reagents; zinc (*26*) and several other metals (*64*) with dithizone; and iron with citrinin (*169*) and with numerous other organic compounds (*277*).

The following papers illustrate different types of processes: iridium in presence of perchloric, orthophosphoric, and nitric acids (*13*); platinum(IV) with chlorostannous acid (*12*); bromine and iodine mixtures in carbon tetrachloride solution (*59*); iodine in chloroform or carbon tetrachloride, along with alcoholic potassium iodide solution (*210*).

The role of heteropoly compounds in absorptiometry has been reviewed (*183*); specific studies on heteropoly systems include arsenic as molybdenum blue (*135*), silicon as molybdosilicic acid (*41*) or molybdenum blue (*86*), and phosphorus as molybdenum blue, using sulfamic acid to eliminate interference by nitrite (*106*).

The thiocyanate ion remains an important reagent, as shown by studies of its use for iron (*19, 235*), for rhenium (*179*), for cobalt (*271*), for uranium (*98*), and for tungsten (*92*).

Reitz *et al.* (*228*) report a study of the application of Fisher's factorial technique to the colorimetric determination of iron by the 1,10-phenanthroline, thiocyanate, and sulfide methods.

Restudy of procedures for organic constituents includes systems represented by the following examples: Folin's method for amino acids (*95*), the U.S.P. method for folic acid (*136*), Pinoff's method for fructose (*262*), and Elson and Morgan's method for glucosamine (*239*).

Others are 8-quinolinol and derivatives with iron(III) (*53, 113*); methanol by oxidation to formaldehyde and reaction with chromotropic acid (*44*); streptomycin and mannosidostreptomycin through the maltol reaction with anthrone (*235*); ethanol through reaction with dichromate and then *s*-diphenylcarbazide (*282*); organic peroxides by reaction with iron(II) and determination of the iron(III) formed with thiocyanate (*151*); and neutral 17-ketosteroids as such (*32*).

New Methods. So many procedures have been published that apparently new space permits little beyond listing them.

Development of colorimetric methods for organic substances has become a major problem in analytical chemistry, both because of the number of different substances and because of their importance. Examples of such systems, with recommended reactants, follow: epihydrin treated with phloroglucinol (*74*); butylated hydroxyanisole with 2,6-dichloroquinonechlorimide (*176*); 2, 3, 5, 6-tetrachloronitrobenzene with acetone (plus tetraethylammonium hydroxide) (*11*); hydrolyzed vitamin B_{12} benzoylated and treated with acetylacetone (*42*); nicotinic acid with cyanogen bromide (*102*) or sulfanilic acid (*260*); 4-aminophenol diazotized and coupled with resorcinol or reacted with 4-dimethylaminobenzaldehyde (*25*); a method for cytochrome oxidase based on rate of oxidation of cytochrome c (*65*); vitamin A with activated glycerol dichlorohydrin (*1*); organometallic compounds, such as phenyl mercuric acetate, with dithizone (*186*); parathion and dimethylparathion saponified to give 4-nitrophenol (*141*); ascorbic acid reduced by *peri*-naphthindantrione (*78*); 2-nitro-1,1-bis(*p*-chlorophenyl)alkanes with ferric chloride (*133*); *sym*-trinitrobenzene with sodium ethylate (*66*); pectic acid with carbazole (*254*); tryptophan with *p*-dimethylaminobenzaldehyde (*252*); oxalic acid by reduction to glycolic acid and reaction with 2,7-dihydroxynaphthene (*216*); methylamine with lactose in alkaline solution (*207*); carbonyl compounds with 2,4-dinitrophenylhydrazone (*165*); various pyridine homologs with a choice of three different reagents (*116*); uroporphyrin by direct measurement at specified wave lengths (*230*).

New methods are plentiful, too, for inorganic systems. Examples employing organic reagents follow: boron with Chromotrope 2B (*115*); sulfide ion with *p*-phenylenediamine (*196*); uranium with oxalohydroxamic acid (*67*); molybdate with catechol (*241*); vanadate with benzoylphenylhydroxylamine (*244*); vanadium with 1,10-phenanthroline (*104*); gallium with 5,7-dibromo-8-hydroxyquinoline (*189*); aluminum with Stilbazo (*158*); germanium with oxidized hematoxylin (*203*); bismuth with sodium thioglycolate (*22*); palladium (*234*) and rhodium (*233*) with 2-mercapto-4,5-dimethylthiazole; gold with *p*-diethylaminobenzalrhodanine (*200*); magnesium with Eriochrome Gray SGL and BL (*147*) or Magneson II (*80*); calcium with murexide (*208*); nickel with *p*-isothioureiodopropionic acid (*269*); chromium (*227*) and manganese (*226*) with ethylenediaminetetraacetic acid; iron with 4-hydroxy- and with 3-carbethoxy-4-hydroxy-1,10-phenanthroline (*110*) and with several other organic compounds (*52, 54*).

Different kinds of processes are involved in the determination of tellurium in the form of the iodotellurite complex (*131*), and of neptunium in perchloric acid solution (*246*).

PHYSICS

The part of an analytical procedure included under measurement of the desired constituent is considered as physics, as the operation involves finding the number of times the standard goes into the unknown. Thus, the subject encompasses the principles, construction, and operation of instruments.

Blottiau's book (*40*), part of "l'Encyclopédie photométrique," deals with color as color, with emphasis upon the ICI recommendations.

Wille (*280*) discusses the theory of absorptiometry, with special reference to the performance of the Beckman, the Pulfrich, and the Hilger instruments. Giles (*99*) surveys basic principles of instruments, including historical developments. Luszczak (*170*) considers the accuracy of absorption methods. Hiskey's proposal to use reference standards of high absorbance has been elaborated with examples of data for three commercial instruments (*119*), and a simple method has been developed for estimating the maximum precision possible (*120*). Shcherbov (*243*) considers deviations from Beer's law resulting from "color saturation."

Certain difficulties have been considered for the measurement of turbid solutions (*134*).

The origin of Beer's law, the basis for calculation of concentration of solutions, has been examined by Pfeiffer and Liebhafsky (*220*).

Miscellaneous Instruments. The principles of various instruments are discussed by Berger and Verbestel (*37*) for the purpose of water analysis.

Nessler tubes are available with interchangeably ground, cap-type stoppers which need not be removed for reading (*211*).

Sols (*249*) suggests a way to eliminate the calculations necessitated in balancing instruments by deviations from Beer's law and from reagent impurities. Watts's "microptic" comparator (*117*) incorporates optically read glass scales to determine the percentage concentration of a solution by comparison with a standard of known concentration.

Potassium dichromate solution is recommended as a permanent standard for bilirubin (*197*) and for homosulfamine (*190*). Other examples of the use of this old device for comparimetric standards are mixtures of cobalt(II) and iron(III) chlorides to match Bogen's universal pH indicator (*88*), buffered potassium chromate for silicon (*8*), fuchsin for epihydrin aldehyde (*74*), and nickel sulfate and potassium chromate for selenium (*164*).

A simple, portable visual colorimeter, of interesting design, has been patented for clinical laboratory work (*112*). The Brociner-Mass precalibrated photoelectric instrument is for the same purpose (*46*). Somewhat similar photoelectric instruments are those of Leitz (*168*) and of the Casbolts (*51*). Another employs a selenium photocell (*118*), and still another an antimony cathode cell (*124*). Ozimov's (*212*) emphasizes simplicity of design. A sturdy sea-going instrument employs an RCA 926 phototube (*90*), and ones for various gases use RCA tubes 926, 929, and 934 (*38*).

A flow colorimeter, including glass filters and two photocells, is designed for work with chlorine (*114*). A differential absorption meter serves for multicomponent mixtures (*61*). The accuracy achieved in analysis with a photoelectric instrument is reported by Musha (*195*).

The principle of double refraction has been applied in the use of electric and magnetic fields as a filtering means to control the color of transmitted light (*17*). Terrien (*264*) used a series of interference filters. Nicholas and Pollak (*204*) studied the effectiveness of British filters for isolating the lines of the mercury arc.

Spectrophotometers. The past year has produced few reports of new, complete instruments. One of significance (*148*) is a recording grating spectrometer with a wave-length scale linear for the range 200 to 1400 mμ. In a review of the principles of absorption spectrophotometry, Arnfelt (*9*) discusses the principal features of spectrophotometers.

Various developments in parts, accessories, and assemblies may be noted. Thompson's instrument (*266*) provides for measuring the fleeting color in the antimony trichloride reaction for vitamin A. An electron multiplier photometer (*81*) may be used as a receptor in assemblies. Use of photomultipliers is considered by Glansholm and Kleman (*101*).

New developments in monochromators include a constant-deviation prism arrangement (*177*), the Farrand double quartz-prism instrument (*82*), a "universal" instrument of wide range with reflecting optics (*217*), and a compact instrument using quartz and polarizers to give a continuously adjustable source with a band width of approximately 15 mμ through the visible region (*50*). Principles for adjusting the Hilger-Müller double monochromator are suggested (*89*). Toporets (*267*) reviewed critically the subject of monochromators.

Of three papers concerning instrumental reflectance standards, one deals with specially prepared barium sulfate (*185*), one recommends an opaque white glass as an auxiliary working standard equivalent to magnesium oxide (*96*), and one reports on the absolute spectral diffuse reflectance of magnesium oxide (*184*).

Robinson and Cole (*231*) reconcile their previously published, divergent views on optimum transmittance in spectrophotometry, but they do not mention the optics of the General Electric instrument.

The practical aspects of the effects of, and tests for, stray radiant energy in spectrophotometers are discussed by Holiday and Beaven (*122*). Two papers deal with the influence of slit width on the results obtained with highly selective systems (*3*, *221*). Steel (*258*) considers the accuracy of polarization photometers, and Caster (*55*) the variability in the Beckman DU spectrophotometer.

The following accessories are of interest: a reflectance attachment for the Beckman B instrument (*31*); a Lucite cell for the anaerobic determination of hemoglobin and oxyhemoglobin in whole hemolyzed blood (*198*); a special aperture for the General Electric spectrophotometer for transmittance measurements of samples of small area (*30*); a 25-cm. cell for the Beckman DU instrument, which by reflection gives a 50-cm. light path (*201*); and an absorption cell for flowing mixtures (*76*). Vacher (*273*) also suggests a type of reflecting absorption cell, designed to achieve a very long light path by means of multiple reflection. He proposes, too, principles and applications of capillary cells 0.5 mm. in internal diameter.

Means are described by Höfert (*121*) for measuring transmittance of industrial glasses in the range 0.2 to 3 microns.

A new spectrophotometer has just been announced for the visible range by the American Optical Co. (C9-1051). It indicates the curve instantaneously on a 5-inch cathode ray tube or records it photographically in a print in about 1 minute.

Stimulus-Measuring Instruments. When the General Electric spectrophotometer is equipped with a special filter in the sample beam, Davidson and Imm's automatic tristimulus integrator may be used for calculations based on illuminants other than illuminant C (*68*).

The Photovolt Corp. has announced a light-measuring instrument with an electron multiplier tube receptor (*222*). A modified Photovolt reflection meter has been tested under various conditions (*71*).

Several tristimulus filter instruments have been described. Included are the Color-Eye matching instrument (*128*), an "industrial" color matcher (*34*), a modified Leitz photometer (*2*), one with selenium photocells (*48*), and one designed by Sziklai (*261*).

APPLICATIONS

From an analytical viewpoint, the general objective of developing methods such as those cited herein is to provide means for determining desired constituents. With colored substances there is often the problem of describing or specifying the color. Both kinds of applications have been considered in the review.

Chemical Analysis. Perhaps of first importance are several new collections of methods for absorptiometric work. Of the books of this nature the new edition of Sandell's well-known monograph (*237*) is likely to be most widely used. The new edition of the American Society for Testing Materials book on the analysis of metals (*5*) contains many photometric methods. The work edited by Rodden (*232*) on the methods of the Manhattan Project includes a general section on photometric methods and scattered procedures for some 20 elements, uranium being treated in most detail. Hunter's book (*125*) is more specialized, being devoted to certain biochemically important systems. Of interest is his use of the word "quantitation." Kingsley's paper stresses the importance of photometric methods in clinical biochemistry (*142*).

Some papers emphasize the nature of a method in connection with its applications. Examples are: precision colorimetry and its application to the determination of manganese (*286*); microspectrophotometry in its application to cytochemical analysis of nucleic acids (*199*); a method based on the determination of absorption relative to an internal standard (*36*); the merits of a ratio method in spectrophotometric analysis (*218*); and the prob-

lem of determining two components in a mixture by absorptiometric means (*20*).

Somewhat different are the two papers by Stearns. The first (*255*) describes the measurement of dye strengths, visually and spectrophotometrically by means of Pineo's formula. The second (*256*) critically evaluates the literature on 32 different kinds of applications of spectrophotometry in textile chemistry, with recommendations regarding the method of interpretation of data for particular purposes.

Applications of heteropoly compounds seem to be increasing. One may distinguish between (1) formation of the compounds to get either central atom (As, Ge, P, Si) or coordinating metal (Mo, V, W) into measurable form, and (2) use of a heteropoly compound as a reactant to produce a color equivalent to some desired constituent, usually through formation of a heteropoly blue system.

Arsenic in biological materials is considered in one paper (*143*) and nickel and copper metal in another (*87*), the molybdenum blue being formed from molybdoarsenic acid. The latter paper deals also with phosphorus and silicon.

For phosphorus the emphasis is on the determination of the element in metals and alloys, five papers being involved (*23, 137, 144, 206, 215*). One paper deals with phosphorus in organic phosphates (*245*), one with hexametaphosphate (*287*), one with phosphorus in equine blood (*7*), and one with special working conditions (*291*).

Likewise, the determination of silicon in metals and alloys seems most important. Of the seven papers concerned (*10, 45, 58, 194, 219, 274, 290*), all but that by Arnfelt *et al.* (*10*) recommend using the molybdenum blue system. Several different reductants are specified.

Potter (*225*) determines silicon in cathode nickel as molybdenum blue, but Guenther and Gale (*108*) use molybdosilicic acid when working with vanadium and uranium, the measurements being made at 390 mμ. Molybdosilicic acid was also used by Aoki (*8*) for silicon in water, and by Devaux (*72*) for noncolloidal silicon in presence of phosphates.

Examples of the application of heteropoly reagents are determination of antimony in copper (*149*); titanium in steel (*150*); phenols (*248*), phosphates in tissue extracts (*107*), and sucrose (*75*).

Two papers describe the use of thiocyanate for determining molybdenum, one in soils and rocks (*276*) and one in plant tissue (*79*). A third concerns the determination of tungsten in cast iron (*279*).

Three papers deal with the use of hydrogen peroxide as the color-forming reagent for uranium in ores and rocks (*275*), for titanium in alloys (*129*), and for vanadium in presence of iron and titanium (*213*).

Several papers describe methods for multicomponent colored systems. Norwitz (*205*) determines aluminum, iron, manganese, and nickel in manganese bronzes; Smets (*247*) determines chromium, molybdenum, nickel, titanium, and vanadium in metals and alloys; and Butts *et al.* (*49*) determine cadmium, chromium, copper, iron, lead, manganese, nickel, and zinc by a combination of methods in industrial wastes.

The following examples illustrate the use of organic compounds as complexants for determining various metals in specific materials: sulfosalicylic acid for aluminum in beryllium (*182*); phenylhydrazine for molybdenum in steel (*14*); thiourea for osmium in organic compounds (*77*); thiazole yellow (*285*) or 8-quinolinol (*283*) with iron(III), for magnesium in plant tissue; diphenylcarbazide for chromium in human blood, urine and tissue (*272*) and in steel (*105*); nitroso R salt for cobalt in beryllium compounds (*209*); and diethyldithiocarbamide for seven metals (*160*).

Reagents studied for copper are rubeanic acid for steel (*187*), diethyldithiocarbamate (*188*) and tetraethylenepentamine (*281*) for aluminum alloys; and 2,2′-biquinoline for plant material (*100*).

Similarly for nickel there are dimethylglyoxime for steel and aluminum alloys (*63*), for beryllium compounds (*209*), and for ores (*60*); and 1,2-cyclohexanediondioxime for calcium metal (*85*).

The following represent determinations based on the inherent colors of the constituents: cerium as trisulfatocerate (*91*); manganese as permanganate (*192*); chromic sulfate isomers (*180*); and mixtures of neodymium, praseodymium, and samarium salts (*284*).

An interesting method for lithium (*202*) is based on precipitating $LiKFeIO_6$ and determining the iron therein colorimetrically.

The determination of cyanides has been studied by Church and Campbell (*62*), and sulfur dioxide in air by Stang *et al.* (*253*). Fluorine in solid halocarbons is determined by its bleaching action on the iron–salicylic acid system (*229*).

Examples of the determination of organic systems through reaction with appropriate reagents include chloronaphthalenes (*159*), volatile esters (*265*), pentoses (*268*), rosin esters (*259*), and starch (*174*).

Color Specification. As more and different colored materials become available, and as their applications increase, there is more and more need to describe and specify color.

Balinkin (*24*) has discussed the physical basis of color, its measurement, and means of specification. A collection of six papers and a bibliography deals fundamentally with color, with particular emphasis on application in architecture (*4*).

Two publications present a wide array of color names. That by Maerz and Paul (*175*) is a new edition of an old, well-known work. The new book, "Descriptive Color Names Dictionary," is a supplement to the "Color Harmony Manual" issued by the Container Corp. of America (*263*). The 775 names included are applied to the Ostwald color chips of the manual.

A "Munsell Color Book in Textiles" has been described (*69*), and presumably it will become available. A federal publication (*83*) contains reproductions of 187 paint colors to provide a means of indicating the colors used in various U. S. governmental agencies.

As a replacement of American War Standards Specification and Description of Color (Z44-1942), new methods of the American Standard Association (*6*) deal with spectrophotometric measurement of color (Z58.7.1-1951), with determination of color specifications (Z58.7.2-1951), and with alternative methods for expressing color specification (Z58.7.3-1951).

A Hunter color-difference meter has been applied to the determination of color specification of tomato purees (*288*). Spectrophotometric measurement of refined sugar in solution established the relationship of the transmittancy at 560 mμ to the monochromatic color analysis values for refined sugars (*289*).

Stearns (*257*) devised a method and apparatus for predicting the color of pigment mixtures.

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INFRARED SPECTROSCOPY

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THE year of 1951 brought few major changes in the field of infrared spectroscopy. Interest in its use in the characterization of organic molecules has continued to grow. Last year's review (*145*) cited 354 references compared with the 419 reported herein.

The Ohio State University Symposium on Molecular Structure and Spectroscopy was attended by 406 persons this year, while the informal international conference on molecular spectroscopy at Basel, Switzerland, attracted about 150 spectroscopists. A number of papers given at this latter meeting were similar to those presented at the Faraday Society Discussions held in the fall of 1950. The Faraday Society papers are reported in this review, inasmuch as the discussion was not published until April 1951.

The National Bureau of Standards, National Research Council, the American Society for Testing Materials, and the Ohio State Symposium committee on cataloging of spectra are cooperating in the collection of literature references and spectra to be made available through the National Research Council. The American Petroleum Institute, Project 44, is now collecting spectra of molecules other than hydrocarbons. Keysort and IBM punched cards using the Wyandotte Chemicals Corp. system (*211*) are being made available at low cost covering the spectra and references in these collections.

A number of reviews on infrared spectroscopy appeared during 1951 (*33, 65, 81, 145, 166, 245, 250, 251, 272, 296, 377, 410*). Strong (*365*) reviewed the history and uses of infrared with emphasis on the experimental phase.

No books devoted exclusively to molecular spectroscopy were published during the year. The second edition of Sawyer's "Experimental Spectroscopy" (*330*) included a slightly enhanced treatment of methods and applications in the infrared field. The McMath Observatory group published an atlas of the infrared solar spectrum (*258*) and a review of this subject (*143*).

INSTRUMENTATION

The most important single development in instrumentation during the year was Walsh's design of multiple monochromators (*403*). This principle may well make obsolete many existing prism spectrometers. The design of infrared photometers has been discussed (*280*) and modern instruments have been reviewed (*353*). Spectroscopic resolution has been related to communication theory (*204*). Mechanical, thermal, and optical properties of prism and window materials have been reported (*70, 304, 383, 387*) and frustrated filters discussed (*36*). Dispersion has been measured with parallel-sided plates (*54*), while the old problem of the optimum optical density has been reviewed (*69, 318*). Infrared refractive indices of liquids have been determined (*187*).

The troublesome task of instrument calibration received attention (*72, 158, 159, 241, 303, 383, 387*). Candler (*60*) has proposed that the reciprocal centimeter be called the Rydberg. While the design and performance of double-beam spectrophotometers has been reported in five papers (*53, 92, 254, 324, 374*), the problem of the absorption of interrupted radiation, so popular in these instruments, is discussed (*73*).

Strong (*372*) and coworkers report a new infrared source, Finkelstein (*117*) reports a new grating mount, and four papers describe new cells (*42, 48, 178, 373*). Two papers describe infrared reflectometers (*281, 355*); an interference spectrometer has been devised (*188*), and three fast scanning or panoramic display instruments have been described (*91, 142, 409*). Beckman instruments have been modified by Kaye (*201, 202*) and Anthony (*12*). A nomograph for the Perkin-Elmer gain control has been devised (*169*).

A ten-channel spectrograph has been made using Golay detectors (*3*), while three papers discuss gas analyzers (*189, 209, 411*). An infrared thermopile has been used in constructing a vacuum gage (*328*); a two-color infrared radiation pyrometer has been devised (*136*); and an infrared radiation converter described (*406*). Infrared microspectroscopy is the subject of seven papers (*21, 38, 125, 148, 277, 310, 364*).

CRYSTALS AND INORGANIC MATERIALS

Ambrose *et al.* (*10*) describe the use of polarized radiation in crystal structure studies, and Hornig (*180*) reviews his low temperature crystal investigations. The reflection spectrum of fused quartz (*55*) and its optical rotation have been measured (*154*). Two papers treat the absorption (*139*) and refraction of calcite (*309*). Studies have been made on rutile (*83*), lithium fluoride (*107*), potassium acid fluoride (*203, 265*), and water of crystallization (*416*). The interpretation of the infrared spectra of mixed crystals has been discussed (*183*).

Hunt *et al.* (*185*) presented 64 spectra of common minerals and inorganic molecules. Studies have been reported on the following inorganic materials: ammonium halides (*41, 180*),

germanium (*356*), nitrosyl chloride and bromide (*57*), P_4 (*32, 155*), lead sulfide, selenide, and telluride (*137*), S_8 and S_2Cl_2 (*32*), SF_6 (*216*), and uranium salts (*127, 320*). Lecomte (*109*) has determined the degree of polymerization of metallic inorganic salts.

QUALITATIVE ANALYSIS

The papers listed in this class include empirical spectra-structure correlations and those which may be useful in general identification. If the main purpose of a paper is plainly vibrational analysis, it is listed in the theoretical and molecular section. Papers dealing with materials of biological nature, or related to these materials, are included in the biological section.

Qualitative studies were made on the following molecules or molecular classes: acetophenones (*361*), acetyl acetonates (*221*), fatty acids and related molecules (*279, 349*), terpene alcohols (*393*), azides (*339*), benzene (*133*), benzene derivatives (*299, 417*), carbethoxythiacyanine (*278*), carbinols (*289*), carbonyl group (*147, 198*), carboxyl group (*95, 118*), cellulose derivatives (*49*), complex and large molecules (*368, 380*), cyclobutyl, pentyl, and hexyl derivatives (*315*), epoxy compounds (*350*), ethylene imine ketones (*82*), glyoxime (*39*), graphic arts (*240*), hydrocarbons (*130-132, 288, 343, 394*), iron carbonyls (*341*), ketones (*123, 156*), keto-lactol tautomerism (*151*), halogen substituted methane (*301*), naphthalene derivatives (*418*), peroxides (*96, 351*), phenols (*128*), phosphorus compounds (*90*), pristane (*298*), propane ring (*195*), pyrimidine (*52*), pyrrole (*196*), pyrrolidine triones (*357*), quinones (*160*), silanes (*66, 332*), sulfones, sulfoxides and disulfones (*11, 88*), sydnones (*110*), terpenoid substances (*61, 297*), thiophosphates (*146*), triazines (*321*), tropolone (*16*), liquid water (*87*), and waxes and polishes (*325*).

QUANTITATIVE ANALYSIS

The general papers in this category discuss methods (*316*), internal standard solid phase analyses (*293*), evaporation errors (*247*), and the principles of precision colorimetry (*175, 176*). A punch card method of calculation of simultaneous equations has been described (*205*). Specific quantitative analyses include: atmospheric gases (*144*), benzene hexachloride (*214, 215*), bromochlorobenzenes (*116*), hydrocarbons (*261*), isotope ratios of C^{12} and C^{13} (*252*), pharmaceuticals (*283*), alkyl phenols (*101*), pregnenolone (*282*), trace components in gases (*99*), methyl deuteride (*51*), nicotinic acid (*388*), nitroglycerin and related products (*292*), phenols and oils in trace amounts in water (*354*), quinine and strychnine (*404*), and water in pyridine homologs (*74*).

HYDROGEN BONDING

Chelation and between-molecule hydrogen bonding studies continue to be popular. Mecke (*246*) reviewed some of his important work, while the Russian school headed by Batuev continued to work on his "frequency-modulation theory" (*24, 25, 149, 274*). Barchewitz (*20*) studied chelation, while Coggeshall (*68*) discussed bonding equilibra. Vol'kenshtein (*401*) reviewed the theories of the hydrogen bond. Francis (*122*) studied the intensities of free and bonded hydroxyl bands in the 3-micron region. Three papers (*193, 389, 392*) reported studies on the overtones of the hydroxyl band in line with the renewed interest in this spectral region. Specific hydrogen bonding studies include: nickel dimethyl glyoxime (*141*), monobasic and dibasic acids (*212, 352*), phenols (*232*), cyclic ethers (*334*), keto-enol tautomerism (*344*), acetoacetic ester (*345, 346*), alcohols (*360*), and muscovite (*391*).

BIOLOGICAL

This year has witnessed an increase in the use of infrared spectroscopy to study natural and biological products. The infrared theory of olfaction has been tested (*119*) and further work must be done before its rejection or acceptance. Three papers dealt with alkaloids (*190, 238, 295*), while bacterial metabolites (*67*), clavacin, and patulin (*150*) were studied. Blood chemistry has even been investigated (*222, 223*) in spite of experimental difficulties. Infrared studies were made on cellulosic materials (*120*), including conidendrin (*362*), while the carbonyl group was determined in such materials (*121, 323*). Ligninlike products were investigated by Nord and Freudenberg (*126*). Chitin was studied (*94*); even two enzymes, cocarboxylase (*224*) and pepsin (*395*), khellin (*18*), nucleic acids (*124*), and rotenone (*86, 399*) had their spectra taken. Wood reported on the microspectrum of living muscle cells (*414*). Papers in the protein field included synthetic polypeptides (*7, 19, 162*), fibrous proteins (*6, 8*), globular proteins (*9*), the peptide link (*63, 255, 256, 390*), chain folding (*112*), amido acids and hydrochlorides (*197*), amino acids (*213*), diketopiperazine (*264*), and the toxic factor from agenized proteins (*348*). Four papers in the steroid field dealt with ethylenic centers (*37*), acetoxy steroids (*194*), normal and isosteroids (*199*), and tocophenols and related products (*322*).

POLYMERS

The following subjects in this category were studied: degradation of polystyrene (*1*), polymerization of styrene and drying oils (*34*), rubber structure (*56*), ethylene polymers (*84*), pleochroism in linear polymers (*140*), analysis of plasticizers for polyvinyl chloride (*163*), acrylic fibers (*182*), charred cellophane (*207*), drying oils (*210*), polynitro phenyl methyl nitramines (*230*), polyamides (*235*), identification of accelerators and antioxidants (*236*), oxidized cellulose (*323*), rubber derivatives (*329*), and polyisoprenes (*369*).

REACTIONS AND COMBUSTION

Ard (*13*) suggested the use of trimethylamine addition products to increase the solubility of materials for infrared studies. Other reactions investigated include anhydrides (*50*), ketones and ethanolamine (*89*), benzene-oxalyl chloride solutions (*327*), peroxide rearrangements (*413*), pyrrole, and other compounds (*419*). Flame or combustion spectra were discussed in two papers (*27, 260*).

ASTROPHYSICAL

Papers in this field include studies on atmospheric N_2O (*2*), OH (*105, 106, 347*), water (*242, 338*), night sky (*248*), aurora (*249*), solar spectra (*257, 336*), atmospheric ethylene (*337*), and a general paper on atmospheric transmission (*134*). Strong (*366*) accounts for the isothermal structure of the stratosphere by pressure broadening of the bands.

ABSORPTION INTENSITIES

General papers in this field include those on the influence of slit width on absorption bands (*5, 290, 412*), the influence of resolution on form and intensity (*294*), and reviews on position and shape of absorption bands (*78, 367*). Pressure-induced absorption was studied by two groups of authors (*396, 407*), while specific intensity studies were made on nitrous oxide (*58*), carbonyl sulfide and acetylene (*59, 317*), carbonyl bearing molecules, (*85*), anomalous intensity distribution in triatomic molecules (*270*), carbon monoxide (*285, 286, 287, 405*), carbon disulfide (*317*), and methane (*408*).

THEORETICAL AND MOLECULAR

This class again has been divided into two groups. The first, the theoretical group, is composed of the more general papers, while the second group is composed of papers primarily treating specific molecules. Overlapping of these groups, of course, does occur.

The theoretical group includes papers on the effect of low temperature on infrared absorption spectra (*161*), the origin of infrared bands (*22*, *157*), the calculation of vibrational frequency change caused by mass, geometry, and potential constants (*29*), and aid in making vibrational assignments (*30*), effects of hyperconjugation on the carbonyl bond (*40*), rotational isomerism (*45*, *305*), determination of normal coordinates (*79*), hybridization and resonance (*103*), bond-bond interactions (*104*), kinetic energy matrix elements (*115*), group theory (*129*), valence symmetry coordinates (*152*), statistical theory of pressure broadening (*237*), mix-crystals (*244*), interaction between nuclear-vibrational and electronic states (*262*), vibration-rotation energies (*271*), the parallel vibrations of linear triatomic molecules (*376*), and van der Waal's forces in potential functions (*386*).

The molecular studies on specific molecules include: acetylpropyl alcohols (*231*), metal acetyl acetonates (*108*), acetylene and substituted acetylenes (*26*, *170*, *172*, *319*), allene (*284*), ammonia and deuteroammonia (*312*, *415*), arsine (*269*), benzene (*181*), fluorinated benzenes (*100*, *273*), boron compounds (*229*, *306*, *333*, *363*), substituted butanes (*331*), trichlorobutene (*164*), 2-methylbutane (*46*), carbon monoxide (*405*), chlorine monofluoride (*268*), chlorine oxides (*113*, *167*), cyanogen and cyanogen chloride (*275*), cyclohexane (*218*, *219*), cyclo-octatetraene (*227*), cyclopentanes (*253*), cycloparaffins (*239*), diazomethane (*80*), dibromoethane (*263*), ethylene (*300*, *319*, *370*), substituted ethylenes (*75*, *217*, *384*, *385*), ethyleneimine (*114*, *177*, *379*), ethylene oxide (*153*, *378*), ethylene sulfide (*379*), formaldehyde (*220*), difluoroformaldehyde (*266*), fluorine monoxide (*192*, *267*), formic acid and formate ion (*375*), germanium tetrafluoride (*62*), hydrazine (*402*), substituted hydrazines (*14*, *15*, *17*) deuterated hydrogen cyanide (*314*), hydrogen fluoride (*342*), hydrogen peroxide (*138*), hydrogen sulfide (*4*, *174*, *228*, *276*), hydroxyl (*179*), hypochlorous acid (*168*), perfluoroalkyl iodides (*165*), isocyanic acid (*173*, *313*), mesitylene complexes (*291*), metallic dimethyls (*43*, *44*), halogenated methanes (*64*, *76*, *77*, *98*, *135*, *234*, *243*, *302*, *398*), methyl and other cyanides (*93*, *397*), naphthalenes (*184*, *335*), nitric oxide (*358*), nitrosyl chloride (*308*), nitrous acid and nitrites (*102*), nitrous oxide (*35*, *171*, *371*, *381*), nortricyclene (*226*), oxalyl chloride (*326*), ozone (*206*, *307*), *n*-paraffins (*23*, *47*), propanes (*71*, *233*), dichloropropene (*31*), triphenylmethyl free radical (*200*), silicon compounds (*135*, *191*, *225*, *259*, *311*, *400*), stibine (*359*), sulfur hexafluoride (*111*), monodeuterotoluenes (*382*), trioxane (*97*), tropolone (*208*), tungsten carbonyl (*340*), and water (*28*, *186*).

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Ultraviolet Absorption Spectroscopy

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THE past year has seen a healthy level of activity, as evidenced by publications on all aspects of the analytical applications of ultraviolet absorption spectroscopy. In particular, the number and variety of the publications dealing with problems of biological or pharmaceutical interest are impressive.

APPARATUS AND GENERAL TOPICS

The development of the potentially important field of spectrophotometry in the vacuum ultraviolet (50 to 200 mμ) has been advanced by a series of three related papers. Tousey and coworkers (*59*) describe a vacuum monochromator, using a 1-meter grating at normal incidence, which is designed for automatic scanning and photoelectric recording. The application of a bismuth-silver thermocouple mounted in the evacuated monochromator to the measurement of the radiant power from a hydrogen arc is reported by Packer and Lock (*46*), who carried out an absolute calibration of this detector. An alternative detector for this spectral range, studied by Johnson, Watanabe, and Tousey (*30*), is a photomultiplier tube whose envelope is coated with a fluorescent material which, under the influence of far-ultraviolet radiation, emits at wave lengths to which the photomultiplier tube is sensitive.

Kaye, Canon, and Devaney (*34*) have adapted a Beckman quartz spectrophotometer for automatic recording. In addition, they replaced the ultraviolet-sensitive phototube with a 1P28 photomultiplier tube which results in an approximately tenfold improvement in resolution. The modified instrument is also adapted for near-infrared spectroscopy.

In a series of three papers, Chance (*15*, *16*) and Chance and Legallais (*17*) describe several types of apparatus for the rapid measurement of small differences in absorption. In one modification for the ultraviolet range, a Beckman quartz monochromator is used as the basic optical component, and special attention is paid to the detector-amplifier system and the control circuits for the radiation sources. In another modification, two monochromators are used with one detector to make simultaneous measurements at two wave lengths.

The radiation emitted by high-pressure xenon arcs was studied by Baum and Dunkelman (*7*) and Anderson (*3*), who worked with direct and alternating current arcs, respectively. These arcs have interesting possibilities as sources of ultraviolet radiation for spectrophotometry. Beale and Roe (*8*) describe a refrigerated cell mount for use with the Spekker photometer and a Hilger spectrograph; this makes possible quantitative measurements down to −165° C. Barer, Holiday, and Jope (*6*) used a combination of the Burch reflecting microscope and a quartz spectrograph to study the variation of ultraviolet absorption with location in a single living cell at a series of wave lengths. A review of gas analyzers utilizing ultraviolet absorption is given by Glasser (*21*).

Caster (*13*) discusses in some detail the instrumental factors which limit the accuracy and precision of data obtained with the Beckman spectrophotometer. Saidel, Goldfarb, and Kalt (*50*) call attention to the possibly misleading effects of stray radiation near the short-wave limit of the Beckman spectrophotometer. They propose a method for correcting for stray radiation which they believe permits the obtaining of reliable data down to 200 mμ. Hiskey and Young (*29*) extended previous work on the use of reference samples whose absorbance is near that of the analytical sample by considering the case in which deviations from Beer's law are significant. They discuss the consequences of the widening of the spectrophotometer slits which is usually necessary to balance the instrument at 100% transmittance with the reference cell in the optical path. A somewhat related but still unusual technique for spectrophotometric analysis is proposed by Jones, Clark, and Harrow (*32*). Their reference absorption is provided by a known solution whose composition can be varied continuously until the difference in absorbance between the analytical sample and the reference solution is zero. When this is done, the effects of deviations from Beer's law, lack of linearity in the photometric scale, and presence of stray radiation are not important. Apparatus for the application of this technique, including an all-glass pump for circulating the reference solution, is described.

An interesting paper on the historical background of Beer's law is contributed by Pfeiffer and Liebhafsky (*48*).

BIOLOGICAL AND PHARMACEUTICAL APPLICATIONS

The precision of a base-line method for the spectrophotometric assay of vitamin A using the absorption band at 328 mμ was studied in considerable detail by Adamson and cooperating analysts (*2*), and the accuracy of the method and its sources of error are treated by Gridgeman (*22*). The value of the factor for converting absorptivity (extinction coefficient) to vitamin A potency in international units per gram is discussed by Stubbs (*57*). Moores and Greninger (*43*) determined trigonelline in coffee by combining a preliminary adsorption fractionation with absorption measurements at 264.5 mμ. Mixtures of aspirin, phenacetin, and caffeine were analyzed by Jones and Thatcher (*33*) by first extracting the aspirin, measuring its absorption in chloroform at 277 mμ, and then determining the remaining two components by use of absorbances at 250 mμ, the phenacetin maximum, and 275 mμ, the caffeine maximum. The hydrolysis of aspirin was studied by Edwards (*20*), who developed a method for the estimation of salicylic acid in the presence of aspirin at any pH by measuring absorption at the isobestic point found at 298.5 mμ. Neuss, Herpich, and Frediani (*44*) present a method for analyzing two-component mixtures of pyrilamine maleate and quinine based on the use of wave lengths of 306 mμ for the latter. Amithiozone (*p*-acetylaminobenzaldehyde thiosemicarbazone) was determined by Levy and Fergus (*38*), who measured absorption at 328 mμ. The combination of chromatographic separation and ultraviolet spectrophotometry was applied by Beroza (*9*) to the determination of the constituents of the alkaloid wilfordine. A quality criterion for medicinal liquid paraffin (white oil) is described by Schnurmann (*51*).

Hiscox (*27*) determined dihydrostreptomycin by heating the sample at 100° in the presence of sulfuric acid and then finding the difference between absorbances measured at 265 and 380 mμ. She (*28*) applied similar methods to the determination of aureomycin and terramycin, obtaining absorbances at 274 and 350 mμ for the former, and 249 and 312 mμ for the latter. Penau and coworkers (*47*) discuss the determination of benzylpenicillin. The absorption spectra of a number of sulfa drugs were studied by Yamabe (*61*). The enzymic metabolism of 3-hydroxyanthranilic acid to quinolinic acid by way of an intermediate was studied by Bokman and Schweigert (*11*), who employed the absorption maxima of 3-hydroxyanthranilic acid at 298 mμ, quinolinic acid at 268 mμ, and the intermediate at 315 mμ. The analysis of 2,4-dinitrophenylhydrazones of some keto acids of biological importance is discussed by Cavallini (*14*). Praetorius (*49*) determined uric acid by measuring the absorption of biological fluids at 290 to 295 mμ before and after the addition of uricase. The determination of ascorbic acid in cerebrospinal fluid by use of the absorption band at 265 mμ was studied by Sophian and Connolly (*55*). They find that the spectrophotometric values are consistently high because of the interference of the albumin present. Spencer and Williams (*56*) determined β-glucuronidase,

using *p*-chlorophenylglucuronide as a substrate, by measuring the absorption of the resulting *p*-chlorophenol in alkaline solution at 245 and 298 mμ. Haas, Sizer, and Loofbourow (*23*) used ultraviolet absorption to follow the kinetics of the oxidation by tyrosinase of tyrosine and compounds containing the tyrosyl group. A review of the ultraviolet absorption spectra of proteins, including possible analytical applications, is presented by Dannenberg (*18*). An unusual application of spectrophotometry is the study of the absorption of living human skin carried out by Edwards, Finklestein, and Duntley (*19*).

INORGANIC ANALYSIS

Tellurium was determined in trace concentrations (0 to 2 p.p.m.) by Johnson and Kwan (*31*), who formed the iodotellurite complex in acid solution and measured its absorption at 335 mμ. Medalia and Byrne (*40*) determined cerium(IV) in the microgram range by measuring absorption at 320 mμ. Telep and Boltz (*58*) find that interfering absorption is minimized in the determination of vanadium at concentrations in the range 0 to 125 p.p.m. by forming peroxyvanadic acid which absorbs strongly at 290 mμ. The determination of low concentrations of beryllium in aluminum is described by Meek and Banks (*41*, *42*). They formed the beryllium-sulfosalicylate complex and measured its absorption at 317 mμ.

ORGANIC ANALYSIS

A method for the determination of low concentrations of styrene in ethylbenzene is presented by Hadden and Perry (*24*), who used a mercury arc as a radiation source. They selected mercury lines in the range 291.6 to 306.7 mμ according to the styrene concentration; the lower the concentration, the shorter is the wave length of the mercury line employed. Newell (*45*) describes the determination of 0.1 to 2% styrene in polystyrene by absorption measurements in the range 250 to 260 mμ. The usefulness of the Cary recording spectrophotometer is pointed out by Kinder (*36*), who refers particularly to analytical problems of petroleum laboratories. Kinder (*35*) also reports a method for estimating the total concentration of alkylbenzenes in petroleum fractions which do not contain benzene, naphthalene, or olefins. This method requires the use of an average absorptivity at 215 mμ, an unusually small wave length. The aromatic hydrocarbons present in some Diesel fuel fractions in the boiling-point range 205° to 265° were identified and partially determined by Adams and Richardson (*1*). A method for the estimation of aromatics in gasoline fractions is given by Shtandel and Shostenko (*53*), and Varsanyi (*60*) discusses the estimation of aromatics in petroleum distillates. Bohon and Claussen (*10*) used absorption measurements to determine the solubility in water of a series of aromatic hydrocarbons.

Hirt and Gisclard (*26*) present a method for the determination of parathion (*O,O*-diethyl *O*-*p*-nitrophenyl thiophosphate) at low concentrations. Using the absorption band at 274 mμ, they find the minimum detectable amount to be 9 micrograms. The absorption of sesamin, a synergist for the insecticidal activity of pyrethrins, at 287 mμ was applied by Budowski, O'Connor, and Field (*12*) to the determination of this compound in sesame oil. Kress (*37*) describes the determination in rubber mixtures of seven common accelerators of the thiazole, thiuram, guanidine, and thiazoline types. Masterbatches containing one or two accelerators were analyzed. Shreve and Heether (*52*) determined the total phthalic anhydride in alkyd resins and other phthalate esters by measuring the absorption at 276 mμ of the acidified aqueous solution of the precipitate obtained in the Kappelmeier procedure. A review of applications of ultraviolet absorption spectroscopy to the study of lignin and related substances is presented by Sohn (*54*). Bailey (*4*) used absorption for the qualitative differentiation of chromatographic fractions of lignins. Ball and Vardell (*5*) describe the analysis of the rosin acids in tall oil by use of absorption in the range 240 to 250 mμ characteristic of abietic-type acids. Hilditch, Patel, and Riley (*25*) have carried out a calibration with pure compounds of a method for the determination of linoleic and linolenic acids based on absorption measurements after alkali isomerization at 268 and 234 mμ. The chemical changes in the catalytic bodying of linseed oil were studied by Maschka and Mendl (*39*), who used ultraviolet absorption to follow the changing concentrations of intermediates in this system.

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X-RAY ABSORPTION

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MOST of the present review is devoted to the determination of tetraethyllead fluid in gasoline by methods involving x-ray absorption.

TETRAETHYLLEAD FLUID IN GASOLINE

The determination of tetraethyllead fluid in gasoline is among the most important routine analyses carried out in the petroleum industry. It exemplifies the advantages and disadvantages of all the common methods involving x-ray absorption—relative to each other, and relative to the chemical and the polarographic. The determination was the subject of an American Society for Testing Materials symposium held in 1950 (*1*), most papers of which appeared too late for the previous review (*30*). These papers are so extensive that it is possible to review only the salient features of each for comparison with those of published investigations not included in the symposium.

The earlier attempts to use x-rays in this determination are described in various papers (*8, 22, 41*). The methods are described briefly in Figure 1 and Table I. The classification of Table I is retained in the subsequent discussion.

Method I [Birks, Brooks, Friedman, and Roe (*6*)]. In principle, the x-ray fluorescence method is simple and specific. The actual situation is more complex, as is shown by the following comments:

The polychromatic x-ray beam from a molybdenum target entered the leaded gasoline sample to excite the characteristic x-ray lines, of which the $L\alpha$ line of lead (1.17 A.) and the $K\alpha$ line of bromine (1.04 A.) were used to establish the amounts present of the two important constituents of one ethyl fluid—namely, tetraethyllead and ethylene dibromide. Intensity measurements (more precisely, measurements of radiant flux or power) were made by taking 1-minute counts on a Geiger counter.

In welcome contrast with another application (*4*), the resolution here was good enough so that counts at the peak intensities (once these were located) and of the background sufficed to establish the concentrations sought. A slight overlapping of the relatively weak $L\beta_4$ line of lead with the $K\alpha$ line of bromine could be regarded as contributing to the background on one side of the bromine line.

Self-absorption, or the decrease in intensity of a characteristic line owing to absorption by the sample of both incident and emitted beams, had to be considered—for example, ethylene dibromide at the same concentration in gasoline will yield the K_α line of bromine at lower intensity if tetraethyllead is also present. The effect of self-absorption can be allowed for if the composition of the ethyl fluid is known or determined, and if suitable calibration curves are available. The contribution of sulfur to self-absorption should ordinarily be negligible.

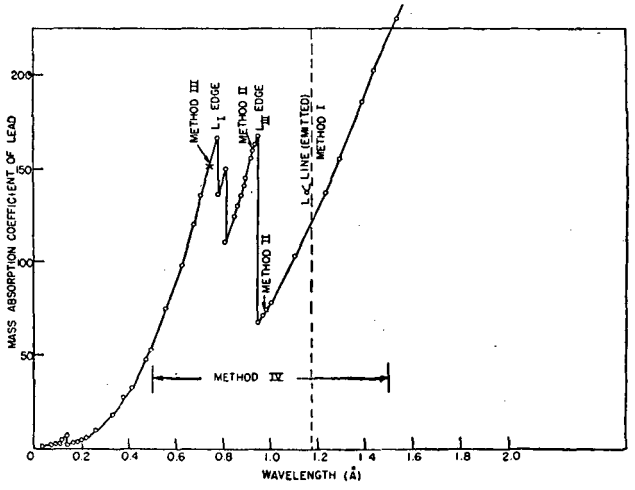

Figure 1. Relationship of Various Analytical Methods to Fundamental X-Ray Data for Lead (*33*)

In Method I, energy of wave lengths below, say 1A, excites the *L* line, whose intensity is measured.
In Method II, absorptiometric data are taken at wave lengths above and below an absorption edge. Extrapolation to the edge gives the change in absorbance from which the amount of the corresponding element is calculated. Several absorbance measurements are necessary.
In Method III, an absorbance measurement is made at a single wave length, preferably one somewhat shorter than that of an absorption edge. Every element, free or combined, in a sample will absorb x-rays, which keeps the method from being specific.
In Method IV, an absorbance measurement is made by use of a beam containing a considerable range of wave lengths. The polychromatic character of the beam can cause complications. The second sentence describing Method III applies here.

The background count is of unusual importance, owing to scattering of the incident x-ray beam by the light elements (carbon and hydrogen) that make up most of the sample. At 4 ml. of tetraethyllead fluid per gallon, the background count (5100 per minute) was half the total, so that the intensity of the L_α line of lead (to which the concentration of tetraethyllead fluid is proportional) was also measured by half the total count. At lower concentrations, the background will be relatively larger. Furthermore, the background will vary with the composition of the sample, especially with the carbon-hydrogen ratio. This variation will ordinarily be negligible but may have to be considered in special circumstances.

Table I. Incomplete Characterization of X-Ray Methods (*33*)

Method	Name	Type	Specific	Measured Intensity	Extreme Voltage Stabilization	Adaptability to Control in Plant
I	X-ray fluorescence	Spectrophotometric	Yes	Low	Desirable	Possibly
II	Absorption-edge	Spectrophotometric	Yes	Low	Desirable	Possibly
III	Absorptiometry (monochromatic)	Spectrophotometric	No	Low	Desirable	Possibly
IV	Absorptiometry (polychromatic)	Photometric	No	Can be high	Sometimes mandatory	Definitely

Table II. Comparison of Chemical, Polarographic, and X-Ray Methods for Determination of Tetraethyllead in Gasoline (22)

	Speed				Relative Cost	
	Elapsed time	Operator time	Samples per day	Accuracy	Equipment	Operator time
	Hours	*Min.*		*Ml. TEL fluid/gal.*		
Chemical	24	40	12	0.04–0.06	1	5.7
Polarograph	1–4	30	16	0.05	10	4.3
X-ray	0.12	7	60	0.10[a]	15	1.0

[a] With base stock constant, or sulfur content known, 0.10 becomes 0.03.

The authors emphasize the importance of selecting the x-ray target so as to minimize scattering.

The authors propose the use of an auxiliary counting system to monitor the incident beam in order to increase precision. This ingenious proposal is likely to be simpler and more effective than attempts to stabilize voltage and current during long counting periods. They also make various suggestions useful for placing their method on a routine basis.

In the opinion of the reviewer, the outstanding advantages of the x-ray fluorescence method are two. First, the mass or volume of sample need not be measured, provided the thickness exceeds the minimum required to give the maximum count at the wave lengths of interest. (The density of the sample may be needed for the calculation of results.) Second, lead and bromine can be determined simultaneously because the method is specific. Birks, Brooks, Friedman, and Roe have pointed out the advantages and disadvantages of this method for the determination of tetraethyllead fluid in gasoline in a valuable exploratory investigation, and an extensive study of the method (modified as they have suggested) under actual operating conditions ought to be undertaken.

Method II [Calingaert, Lamb, Miller, and Noakes (8)]. In cooperation with L. K. Frevel, these authors attempted to apply the method of Glocker and Frohnmayer (*19*), which has been discussed in earlier reviews (*28–30*), to the tetraethyllead problem. Unfortunately, preliminary measurements indicated that the Dow automatic x-ray absorption spectrometer could not resolve satisfactorily the bromine and the lead L_{III} absorption edges (*8*). Preliminary tests indicated that the General Electric XRD-3 spectrometer could accomplish this resolution, and further work with this instrument is in progress.

Method III [Hughes and Hochgesang (22)]. The authors have developed a monochromatic absorptiometric method, which has been employed extensively and successfully for routine determinations of tetraethyllead fluid.

In a modified Norelco x-ray photometer, the absorption cell was placed between a monochromator (rock salt crystal) and the Geiger counter housing. The K_α line of molybdenum (0.71 A.) was used because targets of that metal are available in commercial tubes, and because this line is strongly absorbed by lead, which has its L_I absorption edge at 0.781 A. The time t_0' was determined for 10,000 counts with a nickel standard in the beam. The corresponding time, t, with the sample in the beam was next measured and followed by a subsequent determination of t_0, the latter being done to establish an average t_0 for both this sample and the next. From the ratio $t/\bar{t}_0$, tetraethyllead contents were obtained with the aid of a nomograph. Table II summarizes the authors' evaluation of their method.

Hughes and Hochgesang tested their method on polychromatic beams with a hydrocarbon standard and reached the thoroughly logical conclusion that monochromatic beams are to be preferred under their conditions. The polychromatic beams as generated were of course too powerful for the Geiger counter and had to be stopped down.

Hughes and Hochgesang did not provide for rapid commutation between standard and unknown, so that their method lies closer to the direct than to the comparative method (*43*). With truly monochromatic beams, such commutation is not so important because the effect of voltage fluctuations is less serious (*31*, p. 1011).

Hughes and Hochgesang also demonstrated that tetraethyllead and sulfur could be simultaneously determined by making absorbance measurements at two wave lengths (0.76 and 0.96 A.)—an example of differential absorptiometry with monochromatic beams. This differential method takes advantage of the decreases in the absorbance of lead across the L absorption edges near 0.8 A., and to this extent resembles the method of Glocker and Frohnmayer (*19;* see also above).

Hughes and Hochgesang's way of solving the sulfur problem required the use of a gas-filled x-ray tube with a thorium target, and it will become better adapted to routine applications if a more stable thorium-target tube ever becomes commercially available.

Method IV [Calingaert, Lamb, Miller, and Noakes (8)]. These authors have carried out the most thorough investigation published on the suitability of the General Electric x-ray photometer (*35*) for the determination of tetraethyllead fluid in gasoline under various conditions. Their article should be compared with that of Vollmar, Petterson, and Petruzzelli (*41*), who in 1949 reported results for this determination on such an instrument used without supplementary voltage regulation in a routine petroleum inspection laboratory. Some of these results were presented in greater detail by Vollmar at an ASTM symposium (*40*).

The General Electric x-ray photometer is a split-beam null-type instrument employing the comparative method. It is clear from the nature of the comparative method (*43*) that the use of polychromatic beams introduces complications not present when the beams are monochromatic, and that these complications decrease in importance as standard and unknown approach each other in ultimate composition and in mass, provided commutation between the two is sufficiently rapid.

Calingaert, Lamb, Miller, and Noakes report improving the performance of the General Electric x-ray photometer by making several changes, the most important of which were the installation of a Sorensen voltage regulator and the elimination of the copper oxide rectifiers in the phase-sensing detector bridge circuit.

The performance of the photometer as modified is described in the following quotation:

> The input voltage could be set at a desired voltage with an accuracy of ±0.05 volt and it would remain constant to ±0.10 volt for 0.5 to 3 hours. In fact, it was found that after a warm-up period of 15 to 30 minutes with the x-ray tube operating, the input voltage would register within 0.10 volt of the voltage used the previous day. . . . . The absorbance readings of aluminum versus aluminum were reproducible to ±0.1 mil and those of hydrocarbons versus aluminum to ±0.4 mil for periods of several weeks (*8*).

The authors investigated very carefully the desirability of having standard and unknown approach each other in ultimate composition. They introduced the useful device of employing a solid hydrocarbon block (polystyrene) as a reference standard [for use of solid standards by another laboratory (*26*, *27*), see below]. With this standard, the sensitivity to voltage fluctuations of absorbance measurements on hydrocarbons was reduced tenfold (presumably from what it had been with aluminum as reference standard, cf. 8, Table II).

When an x-ray beam passes through matter, the intensity (strictly, the power) of the beam is reduced owing to true (photoelectric) absorption and to scattering. Although the two processes together determine the value of the mass absorption coefficient (*11*, pp. 515, 535), the latter process is often ignored be-

Table III. Per Cent Absorption Due to Scattering (8)

λ, A.	Mass Absorption Coefficient, μ_m		Mass Scattering Coefficient, σ_m		$\sigma_m/\mu_m \times 100$	
	Carbon	Aluminum	Carbon	Aluminum	Carbon	Aluminum
0.5	0.336	1.950	0.1835	0.1769	54.6	9.1
0.6	0.449	3.226	0.1870	0.1803	41.6	5.6
0.8	0.812	7.318	0.1910	0.1841	23.5	2.5
1.0	1.402	13.95	0.1920	0.1851	13.7	1.3
1.2	2.280	23.68	0.1948	0.1870	8.5	0.8

cause it is unimportant except at low atomic numbers and small wave lengths (*28*, p. 18). Birks, Brooks, Friedman, and Roe (*6;* see also above) have emphasized the importance of scattering in analysis by x-ray fluorescence, where it enhances the background. Calingaert, Lamb, Miller, and Noakes have shown its importance in the absorptiometric determination of tetraethyllead fluid in gasoline.

As these authors point out, apparent anomalies in absorptiometry that have their root in the scattering of polychromatic beams are difficult to disentangle from those caused by changes in the effective wave length of such beams, owing to filtration by the sample. Nevertheless, they succeeded in accomplishing the disentanglement by measuring the absorbance of a 2.7-cm. polyethylene block placed at successively higher levels in the absorption cell of the General Electric photometer. It was shown that the measured absorbance, A, is given approximately by

$$A = a - c(1/D^2) \quad (1)$$

where a and c are constants and D is the distance from the bottom of the block to the x-ray detector. The intercept, a, is the maximum absorbance, which will be measured when the scattered x-rays reaching the receiver are a minimum (D very large). The $1/D^2$ term results from geometrical considerations that govern the intensity of scattered x-rays reaching the receiver. The observed departure from the linear relationship (Equation 1) at decreasing D no doubt results mainly because the intensity of scattered x-rays is highest for small angles (*11*, p. 124).

The calculated per cent absorbance due to scattering as given by Calingaert, Lamb, Miller, and Noakes is shown in Table III. These data are especially significant because it is desirable to carry out absorbance measurements on hydrocarbons at effective wave lengths near 0.5 A., where carbon and hydrogen have closely similar mass absorption coefficients.

Calingaert, Lamb, Miller, and Noakes say in summary: "All apparent anomalies encountered in absorbance measurements are accounted for by scattering and filtering effects." It is the virtue of the comparative method that all these anomalies become negligible if standard and unknown are properly chosen.

Method IV [Levine and Okamoto (*27*)]. This investigation shows that polychromatic x-ray beams can be used successfully with a Geiger counter as detector in the routine determination of tetraethyllead in gasoline, provided the comparative method is employed.

A modified North American Philips 90° Geiger-counter x-ray spectrometer was used, the most important modification being the addition of a sliding dual cradle (*26*, Figure 4) to permit the rapid and reproducible insertion into the polychromatic x-ray beam of either standard or unknown. (This cradle performs the function of the stand in *43*, Figure 2.) Special care was taken to work with a beam of effective wave length 0.53 A., for which carbon and hydrogen have virtually identical mass absorption coefficients. Extensive use was made of polystyrene rods as standards to replace liquid hydrocarbons (see *8* and *26*, p. 701 and Figure 6). The authors give a careful discussion of the various corrections (including that involving the resolving time of the Geiger counter) that must be made, and show how this can be accomplished in straightforward fashion.

Method IV [Liebhafsky and Winslow (*33*)]. After introducing the ASTM symposium, these authors presented published results (*43*) on the determination of tetraethyllead in gasoline by absorptiometry with polychromatic beams according to the comparative method on the laboratory photometer. Furthermore, they demonstrated that differential absorptiometry with such beams could be used to determine both tetraethyllead and sulfur in a hydrocarbon medium. The guiding principle here was that also applied by Hughes and Hochgesang (*22;* see also above). It needed to be demonstrated, however, that the complications possible with polychromatic beams could be reduced so as to make the method practical with a satisfactory detecting system.

Blending. Various authors (notably *22*, *41*) have pointed out that blending operations meet the conditions under which the x-ray absorbance measurements under discussion have proved satisfactory—namely, analysis of leaded gasoline with base stock available for comparison. Liebhafsky and Winslow (*33*, Figure 2) give a schematic diagram of a system proposed by J. P. Smith for controlling the automatic blending of tetraethyllead fluid and base

Table IV. Relative Reliability of Absorptiometric Methods

Reference	X-Ray Method[a]	Detector	Reference Method	No. of Comparisons	Average Deviation	Maximum Deviation[b]		Comments
					Ml. TEL fluid/gal.	*Ml. TEL fluid/gal.* +	−	
(*22*)	III	Geiger counter	Polarographic	25	0.052	0.10	0.16	Assumed S content, 0.07%. Corresponding correction applied.
(*8*)	IV	Multiplier phototube	Chemical	68	0.05	0.12	0.11	Absorbance of unleaded base stock corrected for
(*27*)	IV	Geiger counter	Chemical[c]	9	0.021	0.05	0.02	Sulfur determined and corrected for
(*27*)	IV	Geiger counter	Chemical[c]	54	0.02	Not given		Sulfur determined and corrected for
(*40*)	IV	Multiplier phototube	Chemical[c]	40	0.026[d]	0.10	0.05	Combined experience of two laboratories. Sulfur corrected for
(*33*)	IV	Multiplier phototube	Chemical	14	0.011[e]	0.01	0.11[f]	Laboratory photometer used. Absorbance of unleaded base stock corrected for

[a] See Table I.
[b] X-ray result minus reference result.
[c] A.S.T.M. designation D 526.
[d] Examination of detailed data shows average deviation independent of TEL fluid content.
[e] Data for two base stocks included.
[f] Average deviation 0.004 if this result is ignored.

stock by means of a General Electric x-ray photometer. Other important blending operations could be carried out similarly.

Reliability of X-Ray Methods. Were sufficient data published, it would be highly desirable to calculate the standard deviation for each of the methods of Table I under the best operating conditions. One could then take the position that the results obtained under these conditions can be "guaranteed" to within three standard deviations (*32*).

For Method I, it is of course possible to estimate the minimum standard deviation, s, from the statistical considerations governing the standard deviations of the counting rates (*18*). At 4 ml. of tetraethyllead fluid per gallon, $s = 0.097$ ml. per gallon:

$$s = \frac{4\sqrt{10{,}200 + 5100}}{5100} = 0.097 \text{ ml. per gallon} \qquad (2)$$

where 10,200 is the counts per minute for the sample and 5100 the counts per minute for the background. This minimum s decreases very slowly with the tetraethyllead fluid content so long as the background remains unchanged—e.g., $s = 0.083$ ml. per gallon at 0.1 ml. of tetraethyllead fluid per gallon. Obviously, the precision of the fluorescence method will become prohibitively low as the fluid content decreases.

For the other methods, the problem of evaluating the best precision attainable is more complex. For Method III as an example, this point is made evident by Levine and Okamoto (*27*, Table VII). All investigators of absorptiometric methods agree that the highest precision will be attained when the unleaded base stock is available for comparison, and that uncertainty in the sulfur content of the base stock is the most serious difficulty in other cases. With aviation gasolines, this difficulty is always tolerable because the sulfur contents are low.

Owing to the situation just described, it seems advisable at this time to attempt no more than a summary of what has been accomplished by absorptiometric methods relative to others (see Table IV).

In practically all cases, the average deviation (Table IV, column 6) is comparable with the standard deviation of the reference method. Even though no more precise conclusion can be drawn now, it is clear that the x-ray methods in Table IV have proved successful and should ultimately displace the others except in special cases.

X-RAY FLUORESCENCE

The attractiveness of analytical methods employing x-ray fluorescence is greatly enhanced if high resolution at sufficient intensity can be achieved for the characteristic lines (cf. Method I). When this situation exists, measurements need be made only at the goniometer setting corresponding to maximum intensity and at a nearby setting to fix the background. Otherwise, additional measures must be taken, as by Birks and Brooks (*4*) in their investigation of the zirconium-hafnium and niobium-tantalum systems.

Brissey (*7*) has shown that the General Electric XRD3-unit with fluorescence analyzer, which diffracts the x-rays from the $33\bar{1}$ planes of a bent mica crystal, is capable of resolving the $L\alpha_1$ lines of both tungsten and tantalum from the second-order K_α line of niobium without appreciable loss of intensity. On this spectrometer, therefore, the above-mentioned situation exists not only with respect to niobium and tantalum alone, but with respect to these elements in the presence of tungsten.

Furthermore, at the Thomson Laboratory,

X-ray fluorescence analysis is being used for routine determinations of molybdenum, nickel, cobalt, chromium, and iron in high temperature alloys. Chemically analyzed samples possessing x-ray absorption properties similar to the unknowns are used for standards. Analyses for these elements are made by x-ray fluorescence in about one twentieth of the time required by the usual chemical procedures (*7*).

X-ray fluorescence analysis really began when Moseley showed in 1913 that the characteristic lines emitted by a brass anticathode were stronger for copper than for zinc. Electrons were similarly used to excite characteristic lines in a series of important subsequent researches (*21*), but were gradually replaced by x-ray beams because these were more convenient to use and were less likely to disturb the sample. Recent work by Castaing (*9*) shows that an electron beam is to be preferred in certain cases when an electron microscope is available.

Castaing (*9*) modified an electron microscope by introducing a second electrostatic lens to reduce the cathode image further, and by attaching an x-ray spectrometer to resolve the characteristic lines produced when the electron beam struck the sample placed in the microscope. Outstanding features of the technique are the small size of sample (one micron cube, or thereabouts) that suffices, and the absence of pronounced self-absorption effects. The latter advantage is realized because of the nature of the exciting beam and because this beam does not penetrate appreciably into the sample. Remarkable quantitative results are cited for copper alloys; the results in parentheses are the quotients I_A/I_{Cu} (I_A = intensity of K_α for copper in the alloy; I_{Cu} = corresponding intensity for pure copper) for alloys containing the following weight fractions of copper: 0.01 (0.0099); 0.04 (0.0373); 0.53 (0.504); 0.88 (0.867). This excellent agreement can be further improved by applying suitable corrections. There probably is no better way of analyzing metallic samples for which a point-to-point exploration is required.

MISCELLANEOUS

References are given here to recent investigations of topics treated in previous reviews or reserved for future discussion.

X-ray absorption in the life sciences (*14–17*)
β-ray absorption (*10, 20, 37, 38*)
Uranium in solution by methods involving x-ray absorption (*2, 5*)
Sulfur in hydrocarbons by x-ray absorption (*23–26*)
γ-rays from cobalt 60 (*3, 12, 13, 36, 39*)
Complications possible with polychromatic beams (*34*)
Density measurements in supersonic flow (*42*)
Nondestructive testing methods based on x-ray absorption (*1*)

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X-RAY DIFFRACTION

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IN THE course of the past two years, since the appearance of the last review on x-ray diffraction in this journal, there have been continued developments of apparatus and techniques which have further increased the utility of this tool for analytical purposes. These new developments, together with some of the most recent applications, are reviewed in this paper.

APPARATUS AND TECHNIQUES

The redesigned x-ray diffraction units, manufactured by the General Electric Co. and North American Philips, are now in use in many laboratories. Both of these units are characterized by their highly stabilized x-ray outputs and the sensitive, high resolution Geiger counter spectrometers with which they are equipped. Ohio X-ray, Bedford, Ohio, has also developed a recording x-ray Geiger counter spectrometer. Units such as these are responsible for the increased use of Geiger counter methods compared to the previously favored photographic method for the detection and measurement of x-ray diffraction phenomena.

Hilger and Watts (U. S. distributor, Jarrell-Ash Co., Boston, Mass.) have redesigned their demountable tube x-ray unit and are equipping it with a Geiger counter spectrometer with monitored x-ray beam to compensate for fluctuations. They have also announced a microfocus x-ray unit in which the loading per unit area is about 100 times that of ordinary tubes. This unit promises to be very useful for the analysis of micro specimens.

For those who desire to build their own x-ray units, Garrod (*38*) has discussed the considerations in the design of demountable x-ray tubes. Lees and Armitage (*60*) have presented a circuit for automatic stabilization of continuously pumped tubes. A method has been described for increasing the safe power input into x-ray tubes by improving the water cooling efficiency (*18*).

A great deal of attention has been given to camera modifications and design. Parsons (*72*) has described a method of adapting powder cameras for reflection patterns. An x-ray scanning camera (*96*) has been developed which eliminates diffraction line graininess due to large crystallites.

The realization that many liquid and gaseous compounds may be characterized by low temperature x-ray diffraction has provided a stimulating, rapidly growing interest in this field. A number of new or improved low temperature cameras and techniques have been described (*1, 28, 74*). High temperature cameras have also received their share of attention. Goldschmidt and Cunningham (*39*) and Williams (*105*) have described such cameras. Gordon (*41*) has developed a precision camera and technique suitable for the high temperature measurement of the coefficient of expansion of beryllium. A novel high temperature camera utilizing a thin nickel foil as a combination x-ray filter and furnace has been described by Steward (*86*). The centering and mounting of high temperature camera specimens (*87*) and the calibration and manipulation (*19*) of such cameras have been discussed.

Special cameras have been described by Lawson and coworkers (*58, 59*) for the examination of powder specimens at high pressures.

Alexander (*3*) has presented an analysis of the intensities from slits and pinholes in powder techniques. Considerations in the design of slits have been discussed by Garrod (*38*). Slits are effectively employed as a means of increasing the intensity, particularly where monochromatic radiation is employed. Wrightson and Fankuchen (*111*) have described a simple monochromator designed for powder work. A bent crystal monochromator has been described by Warren (*103*). Dumond (*34*) has developed point focus x-ray monochromators particularly adaptable to small-angle scattering. A collimator producing a beam of small divergence and high intensity (*61*) and an x-ray micro beam for examination of plastically deformed metals have been described (*56*). In the field of small-angle scatter, Bolduan and Bear (*21*) have discussed the effective use of collimating apertures, while Yudowitch (*113*) has evaluated the collimation errors encountered. Double crystal and slit methods for use in small-angle scattering have been compared (*77*).

An improved double crystal spectrometer has been described by Broussard (*25*). Crystals suitable for this application have been discussed (*85*). A new x-ray method involving the use of a double crystal spectrometer for the study of imperfections has been described (*76*). Schulz (*80, 81*) has developed a method for determining preferred orientation in flat transmission and reflection samples using Geiger counter spectrometers.

The preparation of specimens is an important aspect of x-ray diffraction analysis. There have been continued developments in this field. Methods of preparing extruded specimens have been described (*42*, *50*). Two methods (*24*, *36*) have been developed for obtaining x-ray patterns from samples of about 0.001 mg. Beu (*20*) has improved a method for the preparation of powder sample capillary tubes from plastic. Ubbelohde (*98*) has presented a technique involving the use of a low pressure head of water as an aid in the preparation of thin-walled glass capillary tubes. Capillary tubes of varying diameter and uniform 0.01-mm. wall thickness are again available commercially from a source in Germany (Paul Raebiger, Franzstrasse 43, Berlin-Spandau, Germany).

A design has been presented for a sample holder adapted for deliquescent materials (*62*). Singer and Ellinger (*83*) have described techniques for dealing with alloys requiring protective atmospheres. Perrine (*73*) has developed an optical system as an aid for centering x-ray diffraction specimens in powder cameras. A special rotating mount for use with a spectrometer has been prepared for the measurement of crystallite orientation in textile fibers (*82*). The calculation of mass absorption coefficients (*101*) and the absorption correction for encased diffractors for powder work (*78*) have been discussed.

There have been a number of papers relating to the measurement of x-ray intensities. The measurement of intensity is extremely important for the quantitative evaluation of x-ray patterns. Several densitometers have been described (*17*, *26*, *71*, *93*). Considerable work is being done on the use of sensitive crystals such as zinc sulfide and cadmium sulfide (*35*) x-ray detectors. Cochran (*29*) has described a Geiger counter technique for the measurement of integrated reflection intensities. The intensities of single crystal reflections may be measured with a combination two-circle goniometer and x-ray spectrometer (*12*). The Eastman Kodak Co. has available an intensification formula for x-ray films which it is claimed can yield a satisfactory pattern after 15 minutes of normal exposure.

Considerable attention has been given to the measurement of diffraction line shapes with the Geiger counter spectrometer. This method provides a simple and effective manner of measuring crystallite size (*4*, *110*). Wilson (*106*) has treated the influence of size and absorption coefficient on the shape and position of powder diffraction lines. Alexander (*2*) has discussed the geometrical factors that cause line broadening. The effects of crystal and particle size on the x-ray diffraction lines have been considered by Wilchinsky (*104*). Brentano (*22*) has given a quantitative theoretical evaluation of patterns from mixed powders.

The revised ASTM index of x-ray diffraction powder data has been made available. This is an invaluable aid in the identification of unknown compounds. Swanson and Tatge (*92*) have discussed some additions and corrections to the index. Frevel and North (*37*) have advocated the use of tungsten radiation of single wave length for obtaining high resolution powder diagrams.

DeWijs (*33*) has presented a graphical method for indexing cubic materials and for obtaining the unit cell from powder data. The determination of precision lattice constants of noncubic crystals has been discussed by Taylor and Floyd (*94*). The Straumanis method of film measurement, which compensates for film shrinkage and does not require use of the camera radius, has been modified for use without high angle lines (*107*).

APPLICATIONS

X-ray diffraction has continued to be an extremely useful tool for analytical purposes. Its application for the identification and characterization of crystalline compounds has become more widespread.

The papers referred to in this section do not constitute all of those published which have involved the application of x-ray diffraction as an analytical tool. Those chosen for review represent a rather broad sampling of the various applications that have been made.

There have been numerous applications of this tool in the field of inorganic chemistry. Beamer and Maxwell (*15*) have applied x-ray diffraction to the characterization of radioactive materials, including polonium. A great deal of work has been done on the characterization of metal oxide systems, including manganese dioxide (*32*), rare earth oxides (*63*), iron oxides and manganese oxide (*64*), and hydrous oxides and hydroxides (*70*).

Effects of solid solution in calcite (*6*) have been studied, as have solid solutions of bromine and iodine mixtures (*45*). Hoffmann (*51*) has investigated the effect of electrolytes on the x-ray spacings of colloidal samples. A structural investigation of platinum, niobium, and tantalum complexes in solution has been carried out by Vaughan, Sturdivant, and Pauling (*100*).

In the special field of catalysis there have been a number of x-ray studies. The various aluminum oxides and their hydrates have been characterized (*90*). Cobalt-thoria-kieselguhr (*49*) catalysts and Fischer-Tropsch iron (*5*) catalysts have been studied. Particular attention has been given to the study of iron carbides and their role in the Fischer-Tropsch process. The iron–iron carbide equilibrium has been studied (*27*), as has the transition of the Hagg iron carbide to cementite (*30*). Hofer and Cohn have described the analysis of the iron carbide system by x-ray diffraction methods (*47*). Jack (*52*) has presented a structural investigation of the iron-carbon and iron-nitrogen systems.

In the mineralogical field there have been many applications, including x-ray examination of asbestos (*16*) and radioactive minerals (*9*). Barshad (*13*) has studied the effect of interlayer cations on the expansion of the mica-type crystal lattice. Thermal transformations in magnesium chlorite minerals have been investigated (*23*). Van der Marel (*99*) and Jeffries and Jackson (*53*) have discussed the analyses of soils by x-ray diffraction. A rapid x-ray method for determination of silica in industrial dusts has been described (*79*).

High temperature phase changes in metals have been studied by Heal and Mykura (*44*). Tesche (*95*) has investigated the formation of scale on iron between 400° and 700° C. The lattice parameters of martensite and austenite have been given by Mazur (*67*). The measurement of retained austenite in carbon steels (*10*) and steel weld metal (*69*) has been described. A number of alloy systems have been studied, including copper-titanium (*54*) and iron-nickel-chromium (*75*). X-ray line broadening in metals has been discussed by Hall (*43*). The particle size of colloidal gold and carbon black has been measured (*97*).

There has been a very large increase in the number of applications of x-ray diffraction analysis to organic materials. Among the many compounds that have been characterized by x-ray methods are solid aromatic hydrocarbons (*48*), amides of saturated aliphatic acids (*112*), amides and silver salts of fatty acids (*66*), linoleic acids (*108*), saturated 1,3-diglycerides (*14*), amylose complexes (*55*), and derivatives of epoxystearic acids and expoxyoctadecanols (*109*). Methods have been described for the x-ray diffraction identification of alkyl halides as sulfide and sulfone derivatives (*68*) and of *n*-aliphatic aldehydes as 2,4-dinitrophenylhydrazones (*65*). The identification of organic dyestuffs by x-rays has been discussed by Susich (*91*). Solid soaps (*88*, *89*) and thermal transitions in grease (*102*) have been investigated.

There have been numerous applications in the field of high polymers. Synthetic polypeptides have been examined (*11*). The identification of natural and synthetic rubbers has been described (*40*). Arlman (*7*) has compared the x-ray crystallinity of rubber with values obtained by density measurements. The crystallinity of polythene samples has been evaluated (*57*). The molecular weight and size of dried tobacco necrosis protein has been obtained by x-ray methods and compared with electron microscope data (*31*). Yudowitch (*114*) has determined latex particle sizes from x-ray diffraction peaks. Small-angle scattering from polymers (*8*) and cellulose fibers (*46*) has been investigated.

Many organic compounds have been subjected to single crystal x-ray structural analysis. These are not considered here. One example is of particular interest for analytical purposes—namely, the structure of urea-hydrocarbon adducts (*84*). McCrone has continued to present useful crystallographic data on organic compounds as a monthly feature in this journal.

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EMISSION SPECTROSCOPY

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THE principal advances in fundamental research and applications of atomic emission spectroscopy during four postwar years, 1946–49, were reviewed in two reports (*83*, *84*); those reviews are herein extended to the years 1950 and 1951.

Because most of our present-day knowledge of the mechanism of radiation, the structure of atoms, and the properties of atomic nuclei resulted from spectroscopic research it would seem desirable to emphasize basic investigations in these extremely fruitful fields. Since 1940 physical research has been directed principally toward aerodynamics, ballistics, electronics and atomic energy for destructive purposes, and at the present time a large majority of the world's best scientists are still employed in developing military gadgets and "fantastic weapons." However, a few old spectroscopists are still active, and they continue to contribute to standard wave lengths, spectral-line intensities, term analyses, Zeeman effects, isotope shifts, hyperfine structure, and spectra of artificial chemical elements.

STANDARD WAVE LENGTHS

As mentioned before (*84*) artificial mercury obtained by transmuting gold has supplied a new and finer ultimate standard of length (*87*). The manufacture of lamps and the determination of wave lengths of Hg^{198} were described by Meggers and Westfall (*91*). Relative to 5460.7532 A., the wave length of green radiation from Hg^{198}, the wave lengths of 26 other mercury lines were measured to eight figures by Meggers and Kessler (*89*) to serve as secondary standards between 2536.5064 and 5790.6626 A. Attempts to use these accurate measurements for testing the combination principle of spectroscopy were frustrated by errors in the refractive indexes of standard air, until Barrell (*9*) showed that an average of three selected dispersion formulas would fit the observations within the errors of wave-length measurement. For converting standard air wave lengths to vacuum values the use of this composite formula is recommended by Barrell until a better one becomes available.

For metrology two Russian scientists (*10*) reported the wave length (5460.8316$_5$ A.) of a hyperfine-structure component of Hg^{199}. The use of any component of hyperfine structure as a standard of length is impractical and unnecessary. Surely the Russians can make pure Hg^{198} in their uranium piles, and convince themselves that radiations from this isotope are simple and superior to any in nature.

Interferometer measurements of the effective wave lengths of about 60 lines (2247.553 to 5790.6630 A.) characteristic of natural mercury have been published by Burns, Adams, and Longwell (*23*), who also revised the relative values of Hg I terms. They have also reported 8-figure wave lengths for more than 200 lines (3126.1986 to 8919.4987 A.) characteristic of Ne I. The only other recent contribution to precise measurement of wave lengths is the values of 31 Kr I lines (4273.9703 to 6456.2910 A.) measured in vacuum with a reflecting echelon and corrected to standard air (*76*). Standard wave lengths of comparable accuracy are still lacking in the ultraviolet shorter than 2000 A., and in the infrared longer than 10,000 A.

SPECTRAL LINE INTENSITIES

The data of relative wave lengths in atomic spectra have always been vastly more accurate than those of relative intensities. The former have been measured generally to 6 and frequently to 7 figures, whereas intensities have usually been estimated and arbitrarily expressed by one or more figures all of which may be wrong. The first objective physical measurements of spectral-line intensities were made about a quarter century ago to test the quantum theory predictions and rules. These measurements rested upon established principles of photographic photometry and upon the development of recording microphotometers. After the sum rule had been tested in selected multiplets during the next few years, the techniques were adopted by spectrographers to make quantitative spectrochemical analyses, and basic research on spectral-line intensities almost altogether ceased. In recent years there has been a resumption of systematic research on true spectral-line intensities principally on account of demands or encouragement from astrophysicists. Thus, Carter (*25*) has measured relative f values of 47 Fe I lines and applied them to solar and stellar atmospheres. The f values for 430 Cr I lines have been published by Hill and King (*53*), and the relative intensities of more than 1000 Fe I lines from a direct current iron arc were measured with electron multiplier phototubes and electronic ratio recorder by Crosswhite (*34*). Absolute oscillator strengths of chromium and of nickel lines have been determined by Estabrook (*42*).

ZEEMAN EFFECT

To the best of the author's knowledge, few new Zeeman-effect spectrograms have been made since the summer of 1949, but a number of reports based upon earlier observations have been published. Thus Klinkenberg *et al.* (*71*) published magnetic splitting factors (g values) derived from Zeeman-effect observations in Ta I, and Kiess *et al.* (*68*) have done likewise for Ta II. Distorted Zeeman patterns in Mn I have been explained by Catalán and Velasco (*26*) as changes in g values for different magnetic fields. Forbidden components in the Zeeman effect have been discussed by Miliyanchuk (*96*) and by Kiess (*66*).

Unpublished data on Zeeman effect include g values for hundreds of Re I levels and for 20 even and 20 odd levels of Re II, which led to the first classification and interpretation of hundreds of lines in the second spectrum of Re (*88*). Many g values derived from M.I.T. spectrograms of Mn I, Mn II, Co I, Co II, Fe II, Zr II, and Zr III will soon appear in Volume II of "Atomic Energy Levels" now in press (*100*).

TERM ANALYSIS

Despite the limited man power now allotted to this activity considerable progress has been made in the description and interpretation of atomic spectra. The credit in large measure belongs to the compiler of "Atomic Energy Levels" (*100*), who has been most insistent and successful in persuading many older spectroscopists to finish incompleted investigations, undertake new ones, and supply unpublished material. This compilation contains a large amount of new material on the spectra of Cr, Mn, Co, Ni, Ga, Ge, As, Zr, etc. All presently known facts concerning atomic energy levels of 152 spectra emitted by 18 elements (24Cr to 41Cb) are collected in that volume.

An excellent description and analysis of the arc spectrum of fluorine was recently published by Lidén (*75*); it should serve as a model for future reports on the first spectra of halogens.

An outstanding contribution to the structure of rare-earth spectra is now available in the published analyses of the arc and spark spectra of gadolinium by Russell (*113*). These analyses, based on wave numbers and intensities, have led to the classification of 1177 lines of Gd II and 1217 of Gd I, including almost all lines of astrophysical and spectrochemical interest. In Gd I terms of multiplicity 11, the maximum possible in any spectrum, have been identified for the first time.

Extensive analyses, which may be regarded as final, have been published for the first spectrum of arsenic (*94*), and for the third

spectrum of copper (*121*). Progress with the analysis of Ge I (*6*) and of Te II (*79*) has been reported.

The use of lead sulfide cells as infrared detectors has extended the range of accurate measurement of wave lengths beyond the limit of photographic recording, and application to metallic arc spectra in the range 12,000 to 20,000 A. has already paid dividends in new spectral terms of Fe I (*45*), V I (*58*), Ca I (*57*), and Hg I (*56*). That progress is also being made in the extreme ultraviolet is evidenced by publications on Cb V, VI, VII; Mo VI, VII, VIII (*28*); Th III (*69*); and Th IV (*70*).

In spite of the fact that the number of workers on spectral structure is very small there is occasional duplication of effort, as in the case of Ta I (*67, 71*) and U II (*13, 80*). That such duplication is helpful is shown by excellent agreement of two independent investigations of Ta I, and also by serious disagreement in the case of U II. Occasionally a scientific author finds it necessary to disagree with himself; thus the forbidden lines observed in Rb I and first designated as $s - (n-3)f$ transitions are now interpreted as $s - ns$ transitions (*78*).

During the past two years noteworthy contributions to the spectra of artificial chemical elements have been published. The arc and spark spectra of technetium have been disclosed in detail (*90*), and multiplets and terms for both Tc I and Tc II were published (*86*). Although actinium was discovered in 1900 practically nothing was known about its spectra until 1951 when a milligram of artificial Ac was forced to reveal several spectra (*92*). Analysis of Ac II, as of La II, proves the presence of type *f* electrons in excited states, but looser binding is observed in Ac. Measured wave lengths and estimated intensities of 2200 lines of promethium were reported (*93*) but these data are inadequate for term analysis. A preliminary list of about 900 lines (2512 to 7221 A.) observed in spectra of plutonium (*38*) is also inadequate for term analysis and the same must be said of the list of 193 lines (2516 to 4989 A.) reported for curium (*29*). There can be no doubt that the transuranic elements will be subjected to intensive spectroscopic research in the future, provided they are not used to destroy us first.

In addition to supplying data for accurate identification and determination of chemical elements, atomic spectroscopy also serves chemistry in deriving from term analyses values of ionization potentials and binding energies of the valence electrons. In the period covered by this review spectroscopic ionization potentials have been reported as 9.81 electron volts for As I (*94*), 7.45 electron volts for Tc I (*86*), 7.7 electron volts for Ta I (*67, 71*), 28.6 electron volts for Th IV (*70*), and 37.08 electron volts for Cu III (*121*).

The accumulation of such electron-binding energies is sufficient to inspire comprehensive discussions and conclusions in review papers on atomic binding energies (*40*), on spectroscopic and extrapolated ionization potentials of atoms and ions (*43*), on ionization potentials of higher atomic ions (*44*), on estimation of ionization potentials by comparison with neighboring elements (*114*), on binding energies for electrons of different types (*101*), and on theoretical atomic binding energies (*46*). Eventually, if not now, such information will interest chemists because it is basic for the understanding of the formation of chemical compounds.

HYPERFINE STRUCTURE

Since the discovery of uranium fission in 1939 the spotlight has been focused on nuclear physics, and certain aspects of atomic spectroscopy have prospered because they promise to give information about atomic nuclei. These aspects appear in spectral lines either as hyperfine structures or as isotope shifts—two independent indications of interaction between optical electrons and atomic nuclei. 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. Despite great experimental difficulties a large number of nuclear constants is piling up; to cite them all would be most boring, so only typical results of optical methods will be noted here. From hyperfine structure $I = 3/2\ h/2\pi$ for Ba^{135} and Ba^{137} (*7*); $\mu =$ 3.62 nuclear magnetons for Al^{27} (*132*); $\mu = 4.10$ nuclear magnetons for Bi^{209} (*61*); $\mu = 1.8$ nuclear magnetons, and $Q = 0.28$ barn (1 barn $= 10^{-24}$ cm.^{2}) for Br (*111*); $Q = -0.26$ barn for Cu^{63} and $Q = -0.15$ barn for Cu^{65} (*15*); $I = 3/2\ \hbar$ for Ir^{191} and for Ir^{193}, whereas $Q = +0.2$ barn for both (*20*); $I = 7/2\ \hbar$ for both Nd^{143} and Nd^{145}, but $\mu = -1.0$ and -0.62, respectively (*103*); $\mu = 3.3$ nuclear magnetons for both Re^{185} and Re^{187} (*116*); $I = 1/2\ \hbar$ and $\mu = -0.11$ nuclear magneton for Rh^{103} (*73*); $Q = -0.3$ barn for Sb^{121} and -1.2 barns for Sb^{123} (*105*); $I = 9/2\ \hbar$ for Tc^{99} (*64*); $\mu = 5.2$ nuclear magnetons (*65*); $I = 5/2\ \hbar$ for U^{235} (*129*); $I = 1/2\ \hbar$ for Te^{123}, Te^{125} and W^{183} (*47*); $I = 1/2\ \hbar$ for Y^{89} (*31, 74*), and $\mu = -0.14$ nuclear magnetons (*31*); $I = 5/2\ \hbar$ and $\mu = -0.96$ nuclear magnetons for Mg^{25} (*33*); $\mu = +0.6$ nuclear magnetons for Os^{189} (*131*); and $I = 3/2\ \hbar$ for Ac^{227} (*135*).

For Ag^{107} and Ag^{109}, $\mu = -0.087$ and -0.160 nuclear magneton, respectively, was reported (*30*), but experiments with enriched samples changed the assignment of *hfs* components and corrected μ to -0.111 and -0.129 nuclear magneton respectively (*21*). This suggests that other errors of interpretation may exist still undetected. In general, the mechanical moments are most certain and usually exactly half integral, but for Sm^{147} and Sm^{149}, I was first reported equal to $1/2\ \hbar$, later $\leq 3/2\ \hbar$, and finally $5/2\ \hbar$ (*103*), indicating that the interpretation is not always unambiguous.

As a rule the nuclear moments, I, μ, and Q, are observed only for atomic nuclei of odd mass number, but four interesting exceptions have been found. The isotopes Ti^{49}, Cr^{53}, Fe^{57}, and Ni^{61} have odd mass numbers and in sequence differ by only two protons and two neutrons. Even with enriched samples of these odd isotopes all attempts to resolve hyperfine structure in their spectral lines have been unsuccessful (*63, 84*), and these negative results are not explained by the shell models of nuclear structure thus far developed. It must be admitted that theories of nuclear structure are still in their infancy.

In some cases nuclear data derived from hyperfine structures in atomic spectra are supplemented or verified by the structure of molecular spectra. Thus, in band spectra of homonuclear diatomic molecules the successive rotational lines alternate in intensity with a ratio $(I + 1)/I$, and this fact proved that $I = 1/2\ \hbar$ for H^3 (tritium) (*36*) and for He^3 (*39*).

In addition to nuclear data derived by conventional methods of spectroscopy a large number of highly accurate determinations of magnetic moments, gyromagnetic ratios, and electric quadrupole moments have come from microwave spectroscopy and atomic or molecular beam magnetic resonance experiments, but these have been compiled elsewhere (*85*).

ISOTOPE SHIFTS

Different isotopes of any chemical element emit slightly different spectra, the lines being single for even mass isotopes and usually complex for odd mass isotopes. The isotope shifts or energy differences, especially for light elements, are satisfactorily explained by the dependence of the Rydberg constant upon nuclear mass (mass effect), but all departures from this simple effect are blithely blamed on a vague volume effect. For example, the isotope shift $C^{14} - C^{12} = -0.294$ cm.$^{-1}$, and $C^{13} - C^{12} = -0.156$ cm.$^{-1}$ (*55*). These results are consistent with the idea that the isotope shift is strictly a mass effect, since the measured shifts vary linearly with percentage change in nuclear mass. On the other hand the isotope shift $Cd^{110} - Cd^{112} = 0.0135$ cm.$^{-1}$ and $Cd^{110} - Cd^{114} = 0.0295$ cm.$^{-1}$ (*19*), which results are referred to a nuclear volume effect. The isotope shift $Cu^{63} - Cu^{65} = -0.018$ cm.$^{-1}$ (*18*), and for $Ce^{140} - Ce^{142} = 0.054$ cm.$^{-1}$ (*17, 104*). In the resonance lines of Zn (2139 and 3076 A.) the shifts of Zn^{66} and Zn^{68} have been measured relative to Zn^{64}, and after the normal

mass effects are subtracted there are, respectively, residual shifts of +0.010 and +0.030 cm.$^{-1}$ (*32*). In rare-earth spectra isotope shifts $Sm^{144} - Sm^{154}$ have been observed with enriched samples (*122*), and in Gd I the shifts $Gd^{156} - Gd^{158} = Gd^{158} - Gd^{160} = 0.135$ cm.$^{-1}$ (*16*) are said to be uniquely explained by the nuclear volume effect. Likewise the results for Xe^{129}, Xe^{130}, Xe^{131}, Xe^{132}, Xe^{134}, and Xe^{136} (*72*) indicate that the isotope shift in Xe is due to a nuclear volume effect rather than to a mass effect. For heavy elements unequal shifts for equal increments of mass have been reported in osmium (*131*), mercury (*102*), and lead (*81*), but for five uranium isotopes 233, 234, 235, 236, and 238, the isotope shifts of the line at 4244 A. are uniformly 0.82 cm.$^{-1}$ per two mass units (*123*). Obviously, more and better data of isotope shifts are desired.

In concluding this review of recent results of research in spectroscopy mention should be made of the creation of a Joint Commission for Spectroscopy sponsored by the International Union for Pure and Applied Physics and by the International Astronomical Union (*22*). At the organization meeting of this Commission held in Cambridge, England, in September 1950, subcommittees were appointed for listing spectroscopic institutes and main workers and cataloging special spectroscopic equipment; collecting data on research in atomic spectra; collecting data on research in spectra of diatomic molecules; collecting data on research in spectra of polyatomic molecules of astronomical interest; notation in atomic spectra; notation in spectra of diatomic molecules; notation in spectra of polyatomic molecules; and problems to be considered. At the conclusion of that meeting three papers on fundamental problems in spectroscopy were presented—namely, "Fundamental Research in Atomic Spectra" (*85*), "Fundamental Research in Molecular Spectra" (*108*), and "Spectroscopic Problems of Astronomical Interest" (*133*). The next meeting of the Joint Commission for Spectroscopy will be held in Rome, Italy, during September 1952.

SPECTROCHEMICAL ANALYSIS

Publications dealing with sources and uses of atomic spectra in quantitative chemical analysis continue to appear in a steady stream. In addition to hundreds of technical papers, the past two years have given birth to an unusually large number of books on applied spectroscopy. Most of these are good, and some are not so good, but they are all listed here, without prejudice, by title: "Practical Spectroscopy" (*24*), "Chemische Spektralanalyse" (*119*), "Spectrochemical Analysis" (*2*), "Practical Applications of Spectrum Analysis" (*37*), "Spectrochemical Procedures" (*50*), "Optische Messungen des Chemikers und des Mediziners" (*77*), "Principles and Practice of Spectrochemical Analysis" (*106*), "Experimental Spectroscopy" (*115*).

The scope of this article does not permit the listing of all recently published papers on applied spectroscopy; this will be done in Part III of "An Index to the Literature of Spectrochemical Analyses" (*118*). In this article only a few of the recent papers are cited to illustrate technological advances and applications.

Further efforts to improve spectroscopic light sources have brought forth an induction-heater source (*112*), a double-arc source (*120*), and an electronic time-switching device (*35*) designed to select arc-like spectra from spark sources. Electronic devices have become universally popular and in many spectrographs the conventional photographic plate has been displaced either by Geiger-Müller counters or by electron-multiplier phototubes. These devices eliminate photographic exposing, processing, calibrating, and measuring; they make the spectrometers essentially direct reading. Because electron-multiplier phototubes also have defects, attention is called to two papers discussing their properties and uses in spectroscopy (*48, 136*). Mention of auxiliary apparatus is here restricted to an improved electrode holder (*126*), and a novel step sector for astigmatic spectrographs (*134*).

Spectrochemical analysis of metallic alloys has become a universal routine in production control, but many technical papers on this subject continue to flow from industrial laboratories. Of special interest are the determination of carbon (*14*) and phosphorus (*49*) in steel, and the quantitative spectrochemical analysis of Cr—Ni (18—8) stainless steel (*41, 51, 139*), including the determination of tantalum and columbium in stainless steel (*110*). Spectrographic analysis applied to pure metals (Ag, Al, Au, Cu, Mg, Pb, Pt, and Zn) shows that pure metals are really rare (*124*).

Spectrochemical analysis in metallurgy is perhaps too commonplace to be interesting but geology gives examples of application to silicate rocks (*3, 4*), the determination of tin and indium in mica (*5*), impurities in sulfides of silver (*8*), or in coal and coal ash (*59*), and three methods for the spectrographic determination of uranium in ores (*127*), which may lead to a cash prize if enough uranium is found.

Applications of spectrochemical analysis of trace elements in botany include cinchona leaves in India (*82*), the spectrographic analysis of minute quantities of metals in plant materials in Japan (*107*), the application of spectrochemical analysis in fruit research in South Africa (*128*), the distribution of rubidium in 16 families and 366 plant species in France (*11*), and trace metals in cotton fibers in the United States (*52*). Also recently reported are determinations of nutrient-element composition of leaves from apple, peach, cherry, and pear trees (*62*), and alkalis in tobacco leaves (*138*). These examples prove that spectrochemistry of plants is fairly widespread, if nothing else.

In the field of biology, the spectrographic determination of lead in blood was reported in two papers (*27, 117*); it was found that values below 100 γ Pb per 100 ml. of blood are normal and those above 300 γ Pb per 100 ml. of blood are pathological even without clinical symptoms. In human blood the relative variations in rubidium are greater than those in potassium and sodium (*12*). The simultaneous spectrochemical determination of sodium, potassium, calcium, magnesium, and phosphorus in blood serum needs only 0.1 ml. of sample (*109*). Spectrochemical values for sodium, potassium, iron, magnesium, and calcium in normal human plasma (*125*) are, for example, 142 $\pm$ 1.8 milliequivalent per liter by flame photometric and 145 $\pm$ 5.5 by spectrographic methods. Excellent results for calcium, sodium, and potassium in milk are obtained by flame photometry (*60*). Quantitative spectrochemical analysis of liver and blood (*1*) has led to a possible correlation between the zinc content and cancer. One problem of great current interest is that of determining cobalt, which is known to be part of the molecule of vitamin B 12 and, for this reason, is presumed to be present in blood. It escapes detection, however, even though the spectrographic technique is sensitive to a few parts of cobalt per billion of blood (*97*). Living or dead, the strontium content of human bones ranges from 0.016% in fetal specimens to 0.024% in adults, including cadavers (*54*). Nineteen mineral elements were determined spectrographically in beef, but no significant differences could be detected between seven different grades of beef ranging from "choice" to "bull" (*98*).

The following are unusual applications. A spectrographic analysis of varnish from the Prince Gunski Stradivarius cello made in 1697 determined aluminum, silicon, calcium, iron, magnesium, sodium, lead, copper, silver, tin and boron, in agreement with other analyses of old Italian brown varnishes, the colors of which are attributed to a small amount of iron rosinates that darken with time (*95*). The isotope shift in the 6707.8 A. resonance line of lithium has been used for the assay of isotopes of Li^6 and Li^7 (*130*). This is the third element to which spectrochemical analysis of isotopic composition has been applied, the previous ones being hydrogen and uranium.

It might be concluded that emission spectroscopy is now applicable to the elementary analysis of almost all materials, and this is largely true. The only apparent exceptions are gaseous mixtures, and even these can be analyzed spectrographically, as

is shown by recent reports on the determination of nitrogen in argon (*99*), and of carbon dioxide and nitrogen mixtures (*137*). It may be that new techniques with electrodeless discharge lamps, and ultra high-frequency excitation which eliminates "clean-up," will solve the present problems in spectrochemical analysis of gaseous mixtures.

There are indications that many applications of emission spectroscopy to chemical analysis have been published in the Union of Soviet Socialist Republics; none of these has been cited in this review because the language barrier and two "iron curtains" make it practically impossible for us to read the original papers even if they contain anything worth reading.

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MASS SPECTROMETRY

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TWO previous reviews of the literature on mass spectrometry have appeared in this journal. In the interval since the last review (*177*) the large number of publications indicates a continuing increase in the use of the mass spectrometer in fundamental and applied research. Improvements in instruments and techniques have contributed to an increase in the speed and accuracy of analysis for the chemist and have also extended the field of application. An increasing number of laboratories are exploiting the mass spectrometric techniques for the study of dissociation processes and of reaction kinetics. As in the past, the work in physics promises the development of new methods of ion analysis which will find future application in chemistry. In addition to this, the overlapping interests of chemists and of physicists in mass spectrometry make it desirable that this survey be as complete as possible for both groups.

INSTRUMENTS, METHODS, AND TECHNIQUES

Descriptions of analytical instruments of the magnetic deflection type which incorporate various modifications, improvements, and special features have appeared in the literature (*5, 10, 15, 20, 61, 111, 113, 185, 196, 207, 209, 210*). The group working with Urey has described the experimental arrangement whereby it has been able to attain high precision in making relative measurements of isotopic abundance (*123*). Two new instruments for doublet measurements have been described: that of Duckworth (*50*) and that of Nier and Roberts (*140*) in which high stability is attained by means of an auxiliary ion beam. Four papers deal with source problems (*7, 16, 26, 153*).

A continuing interest in radio-frequency and time-of-flight mass spectrometers which involve no magnetic field is apparent (*22, 23, 84, 108, 174*). A similar interest has continued in the timing instruments that are based on the principle of cyclotron resonance (*18, 91, 98, 179, 180, 183, 184*).

Leak detectors of various designs are detailed (*161, 193, 217*). The problems in sample systems of avoiding stopcock grease and of handling liquid samples have been solved in several ways (*45, 73, 87, 156, 160, 220*). Other special topics are covered: mass indicator (*31*), electron current regulator (*32*), leaks for controlling flow (*66, 80*), precision slit (*65*), and metal gasket (*89*).

Geerk and Brix have studied the blackening of photographic plates by protons through the use of a mass spectrograph of the Thomson type (*75*).

ION OPTICS

The references listed in this section are concerned primarily with theoretical studies aimed at improvement of the focusing properties in ion sources (*34, 130, 215*) and analyzers (*33, 35, 86, 88, 99, 133, 150, 169, 194, 212*). Most of them treat variations of the instruments employing sectored magnetic fields because of the greater design flexibility permitted by tilting or shaping the boundaries of the magnetic field through which the ions pass. The aim of these efforts has been to achieve wider angle focusing (second or higher order) or two-directional focusing. Ploch and Walcher (*154*) have studied the effect of the stray field and the latter has reviewed the ion optics involved in mass spectrometry (*214, 215*). Sakai has suggested an arrangement which is presented as a perfect velocity-focusing mass spectrometer (*170*). Svartholm (*195*) describes a combination of crossed, nonuniform electric and magnetic fields by which it is expected to achieve both two-directional and velocity focusing of ions.

IONIZATION AND DISSOCIATION BY ELECTRON IMPACT

Much effort has been devoted to obtaining mass spectral data of a wide variety of compounds including isotopically substituted molecules, organometallics, isomeric hydrocarbons, and compounds of high molecular weight. Condon (*41*) and Condon, McMurry, and Thornton (*42*) have reported the mass spectra of some hexa-, hepta-, and octadeuterated derivatives of propane. Dibeler and Bernstein (*44*) have measured the isotope effect on dissociation probabilities in the mass spectra of chloroform and

chloroform-*d*. Schaeffer (*171*) has described a general method for calculating the effect of isotopic substitution on mass spectra of molecules. All of the deuteromethanes were synthesized and the mass spectra obtained by Dibeler and Mohler (*46*). Mass spectra of N^{14}_2, $N^{14}N^{15}$, and N^{15}_2 were reported (*47*), as well as the dissociation probabilities of H_2, D_2, T_2 (*48, 173*) and HD, HT, $C^{13}O$, $C^{13}O_2$ (*48*). The spectra of diborane-d_6 and of ethane-d_6 were measured (*49*) and compared with the spectra of the normal molecules. Norton (*142*) compared the spectrum of $B^{10}_2H_6$ with the calculated spectrum of normal diborane.

Stevenson and Wagner (*191*) obtained the spectra of C_1 to C_4 monodeutero paraffins and compared these with the corresponding spectra of the normal hydrocarbons.

Baldock and Sites (*6*) studied the dissociation of some nickel carbonyls. Brannon, Dozier, and Carr (*25*) reported studies of a series of organic phosphorus compounds.

Mohler and coworkers have reported studies of a series of isomeric hydrocarbons including C_5H_8 isomers (*126*), *cis*- and *trans*-decahydronaphthalene (*128*), and the isomeric nonanes (*129*). The total ionization of hydrocarbons was studied by Mohler, Williamson, and Dean (*127*).

O'Neal and Wier (*147*) modified a standard Consolidated mass spectrometer to permit the introduction of completely vaporized samples of hydrocarbons up to C_{40} and to provide a mass range up to approximately $M/e = 600$.

Ewald and Henglein (*68*) observed ion dissociation with the aid of a parabola spectrograph. Sites and Baldock (*178*) reported ionization and dissociation studies. Langer (*117*) discussed rearrangement peaks observed in some mass spectra of hydrocarbons and oxygen-containing compounds.

The effect of temperature on the mass spectra of a number of hydrocarbons was studied by Berry (*13*) and by Reese, Dibeler, and Mohler (*159*).

Berry (*14*) reported on the effects of initial energies on mass spectra and discrimination effects in the mass spectrometer.

Studies of negative oxygen ions were reported by Watanabe and Mida (*219*). Dukel'skiĭ, Zandberg, and Ionov determined the negative ion spectra of the chlorides of rubidium and cesium (*60*) and of the chlorides and iodides of lithium, sodium, and potassium (*59*).

Bates, Fundaminsky, Leech, and Massey (*8, 9*) have published mathematical papers on the excitation and ionization of atoms by electron impact, discussing in particular the Born and Oppenheimer approximations. Mitchell and Coleman (*125*) discussed the effect of impact parameter, distribution of electron energy, and transition energy on appearance potentials of hydrocarbons. Warren (*218*) described a graphical method of extrapolated differences to evaluate appearance potentials. Fox, Hickam, Kjeldaas, and Grove (*71*) have reported an important advance in the technique of measuring appearance potentials. By using a pulsed electron beam and appropriate stopping potentials to obtain a nearly monoenergic electron beam, they have succeeded in making direct measurements of ionization probabilities and appearance potentials.

Tickner, Bryce, and Lossing (*201*) reported measurable differences in the appearance potentials of the deuteromethanes, the difference increasing with the extent of deuteration. Burhop, Massey, and Watt (*28*) studied the ionization and dissociation of uranium tetrachloride and hexafluoride. Appearance potentials of some metastable transition ions found in hydrocarbon mass spectra were measured by Fox and Langer (*72*). Geerk and Neuert (*76*) reported the ionization and dissociation of methane, methanol, and methylal. Appearance potentials of the several ions in germanium hydride were measured by Nève de Mévergnies and Delfosse (*137*). Osberghaus (*149*) reported the appearance potentials of electron impact products of boron trichloride and trifluoride. Values of the ratio B^{10}/B^{11} were also given for a number of sources of boron. Ionization and dissociation of cyanogen, hydrogen cyanide, and cyanogen chloride were studied by Stevenson (*188*). Kambara measured appearance potentials of hexane, cyclohexane, and benzene (*101*), *n*-propyl alcohol (*102*), isopropyl alcohol (*103*), and acetone and acetic acid (*104*). Field (*69*) reported a new calculation of the latent heat of sublimation of carbon and the first C-H dissociation energy in methylene. Field and Hinkle (*70*) measured the ionization potential of cyclopropane.

APPLICATION TO PHYSICAL CHEMISTRY AND CHEMICAL KINETICS

The kinetics of the pyrolysis of diborane was studied by Bragg, McCarty, and Norton (*24*). Coggeshall and Kerr (*38*) reported mass spectrometric studies of thermal decomposition products of various hydrocarbons. Coggeshall (*37*) described the role of mass spectroscopy in the determination of organic functionality. Wall and Moore (*216*) studied the pyrolysis of 50-50 mixtures of ethane and ethane-d_6. Norton (*143*) presented evidence for the existence of a new boron hydride, possibly B_9H_{13}, in diborane stored for a long time at −78° C.

The important application of the detection of intermediate reaction products by mass spectroscopy was discussed by Elteton (*62*). The method was based on the fact that in general the ionization potential of radicals is lower than the appearance potential of the same ion produced from a parent by electron impact, thus permitting the separate detection of radicals.

Several papers reported mass spectrometric studies of various nickel-catalyzed reactions. Kemball (*110*) studied the reaction of methane and deuterium on evaporated nickel catalysts. Taylor and Dibeler (*197*) reviewed recent mechanisms proposed for the catalyzed reactions of unsaturated hydrocarbons with protium and deuterium and presented some new experimental results. Wright and Taylor (*221*) reported on the interaction of methane and methane-d_4 on nickel and on the state of the nickel catalyst. Turkevich, Bonner, Schissler, and Irsa (*206*) discussed the use of stable and unstable isotopes and the application of the mass spectrometer to catalytic research.

Fractionation of the carbon isotopes in decarboxylation reactions was studied by means of the mass spectrometer. Bigeleisen and Allen (*17*) reported on the relative rates of decomposition of $1\text{-}C^{12}$ and $1\text{-}C^{13}$ trichloroacetate ions. Bothner-By and Bigeleisen (*21*) studied the relative rates of decomposition of carboxyl-C^{12} and -C^{13} mesitoic acids. Lindsay, Bourns, and Thode (*120*) reported on the carbon 13 isotope effect in the decarboxylation of *n*-malonic acid. Lindsay, McElcheran, and Thode (*121*) studied a similar reaction of oxalic acid.

Landeen, Farnsworth, and Sherburne (*116*) described the application of a mass spectrometer to the study of surface reactions at low pressures. Plumlee and Smith (*155*) reported a preliminary study of sublimation characteristics of oxide cathode materials and Stier (*192*) studied the activation of barium oxide cathodes.

Tickner and Lossing (*202, 203*) have applied the mass spectrometer to the measurement of vapor pressures of a number of light hydrocarbons and carbon dioxide in the range of 0.001 to 10 mm.

ANALYTICAL APPLICATIONS

Rock (*166*) has stressed the value of mass spectrometric analysis in the qualitative resolution of mixtures. Spectra of 279 compounds were tabulated and classified. Various means of identifying compounds in mixtures were discussed. These included the use of isotope abundance ratios, the presence of ions resulting from metastable transitions, etc. Burkhard and Norton (*29*) applied the mass spectrometer to the qualitative analysis of organosilicon compounds and polymers. Univalent hydrocarbon radicals directly attached to silicon were connected to the related hy-

drocarbon gas by heating with concentrated sulfuric acid and admitted directly to the mass spectrometer. Qualitative analysis aided by a punched-card catalog of mass spectral data was described by Zemany (*222*).

Several papers reported methods of detecting trace amounts of impurities, particularly in samples of hydrocarbons highly enriched in C^{13} and in deuterium. Methods described by Honig (*92*), Stevenson (*189*), and Stevenson and Wagner (*190*) were based on the properties of the initial portions of the ionization efficiency curves of the molecule ions and of the fragment ions. Rollmann and McMurry (*168*) used parent-peak intensities as a basis for estimating purities of deuterium substituted compounds. Happ, Stewart, and Brockmyre (*81*) reported procedures for determining most of the ordinary contaminants in air (except carbon monoxide) in quantities below 100 p.p.m. Quantitative microanalyses of mixtures of nitrogen, oxygen, and hydrogen were described by Kambara (*100*).

Two methods of analysis of particular interest to petroleum laboratories were reported. Brown (*27*) described the analysis of gasolines in which compound types were determined. The procedure was considered extendable to type analysis of higher boiling fractions and to nonhydrocarbons. O'Neal (*146*) described the use of mass spectrometric and infrared data for the analysis of certain hydrocarbon mixtures.

Gorman, Jones, and Hipple (*77*) described the isotopic and chemical analysis of solids by means of a mass spectrometer. Details were given of an instrument and techniques suitable for the analysis of alloys. A report from the Kellex Corp. (*109*) described means of introducing solid samples into an ionization chamber. In one, the sample was deposited on a metal tape that passed through a series of vacuum locks. A model was built and tried with some success but not in conjunction with a mass spectrometer. A design was also given of a possible method of inserting through multiple locks a filament or furnace for vaporizing solid samples.

Shepherd (*176*) has discussed the reproducibility and the accuracy of the mass-spectrometric method of analyzing a standard sample of a carbureted water gas. A comparison was also made (*175*) of the analysis of the same standard sample by mass spectrometric and by chemical methods. The accuracy and the precision of analysis of light hydrocarbon mixtures were discussed by Starr and Lane (*187*). Conclusions were drawn concerning the relative merits of mass spectrometric, ultraviolet, infrared, low temperature distillation, and chemical methods.

MASS MEASUREMENT

The work on the measurement of packing fractions which in the past has been associated with the names of Aston, Bainbridge, Dempster, Mattauch, and others was interrupted during World War II and this field has only recently grown in activity with the completion of instruments that have been under construction for the past few years. Duckworth and his coworkers have reported measurements on many elements in the heavier mass range with their Dempster-type instrument (*51–58, 186*). Nier and his Minnesota group have reported exceptionally fine results using their new method in which the ion beam is detected electrically (*40, 79, 141, 165*). Mattauch and his associates have increased the resolution of the Mattauch-Herzog type of instrument and have so greatly improved their techniques that they have been able to report very good progress in improving on their earlier excellent measurements. Ewald has reported new measurements of many doublets and mass values through mass 40 (*64, 67*). The Japanese school has been active in improving the resolution of the Bainbridge-Jordan type of instrument as evidenced in the recent communication of Ogata and Matsuda (*145*). Bainbridge discusses the isotopic weight of helium (*4*) and Hays, Richards, and Goudsmit (*83*) report measurements with their time-of-flight instrument.

ISOTOPIC ABUNDANCE

Discrimination by the mass spectrometer has always been a problem in the determination of the true relative abundance of the isotopes in a given sample. Many papers in the past have discussed the causes of these discriminations and recommended techniques for minimizing their effects. Nier (*138*) has described a method of measuring the relative abundance of isotopes, in which the discrimination in his apparatus was experimentally determined by calibration with known synthetic mixtures of the previously separated isotopes of an element. Probably the most important element which he studied was oxygen and his results provide the most accurate value of the constant of conversion from the physical to the chemical scale of atomic weights. This work also re-emphasizes the effect on the conversion factor of the variations in the abundance of the isotopes of oxygen from different sources. Data on the abundances of the isotopes as well as the variations of these in nature have been increased by the research of many workers (*1, 3, 19, 39, 78, 82, 85, 94, 118, 119, 122, 139, 148, 151, 172, 181, 182, 198, 200, 204, 208*).

The authors have been much interested in a paper by Wahl (*213*) which only recently came to their attention. This describes a Mattauch-Herzog instrument and its application to the study of the age of various minerals. Although this work appeared long before the period covered by this survey, it is included now because this description of a Mattauch-Herzog instrument appeared in a journal unfamiliar to many readers.

NUCLEAR PHYSICS STUDIES

The use of the mass spectrometric method for the separation of isotopes has been described in four publications (*12, 43, 106, 107*). A large number of papers give an account of the research on isotopes separated in this manner and others relate the success in identifying the products of nuclear reactions while providing a means of studying nuclear processes (*2, 11, 93, 95–97, 105, 114, 115, 134, 158, 162–164*).

REVIEWS

Since the appearance of the previous bibliography (*177*), a surprising number of general review papers have appeared in print (*30, 36, 63, 74, 90, 112, 124, 132, 135, 136, 152, 157, 167, 177, 199, 205, 211*). For the most part, these have stressed chemical and isotopic analysis.

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ORGANIC POLAROGRAPHY

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STUDIES in the field of organic polarography in the past two years have extended the use of this method to a variety of new groups. Contributing to this increase has been the greater use of solid electrodes. More electrode reactions have been verified by large scale electrolysis under controlled conditions with the isolation of products. In general, conclusions drawn from such experiments are in good agreement with the reactions at the electrode. Occasionally the products are different, as the large scale experiments involve rapid stirring and are not dependent solely upon a diffusion process. Intermediates, therefore, may be removed from the electrode surface to the solution where dimerization, disproportionation, or rearrangement may occur. The possibilities of the cathode-ray polarograph in the organic and reaction kinetics fields have been indicated (*178*). An extensive list of half-wave potentials of organic compounds with the conditions used has been published (*218*).

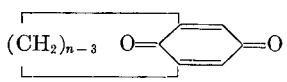
As in the past, most of the studies have been carried out in mixtures of organic solvents and water. The number of anhydrous solvents employed has been small and consists of methyl Cellosolve (*142*), methanol (*152*), ethanol, 1-propanol, butanol, ethylene glycol, glycerol, and solutions of some of these with benzene or dioxane (*46*). The diffusion current was found to be inversely proportional to the square root of the viscosity of the solvents, and the waves became more drawn out as the amount of alcohol was decreased in dioxane mixtures with methanol, ethanol, and 1-propanol (*46*).

As supporting electrolytes the tetraalkylammonium salts have continued to be useful. Their range has been found to be dependent upon their purity. It has been suggested that catalytic hydrogen waves are responsible for the wave observed with these salts and not the reduction of the cation (*180*). Directions are given for the preparation of tetramethylammonium chloride for polarographic analysis (*7*).

REVERSIBLE SYSTEMS

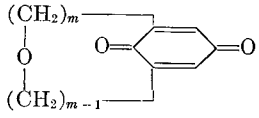
The polarographic method has been used to determine the oxidation-reduction potentials of a number of quinones and related compounds.

Values have been obtained for a number of polymethylene quinones having the following structures and compared with that of 2,6-diethylbenzoquinone in order to determine whether or not the rings were strain-free. Oxidation of the corresponding hydroquinones at the same point established the reversibility of the system (*146, 148, 149*).

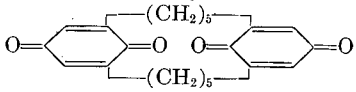


n = 9–19

I



II m = 4–5, m = 10



III

The E_0 for bis-(2,4,5-trimethylquinonyl)methane was found to be 0.457 volt and very similar to that of duroquinone (*177*).

The polarographic method has been used to study qualitatively the reaction of benzoquinone with proteins, polypeptides, and amino acids (*209*), and indicates that quinones react with or are destroyed by glycolytic enzymatic medium (*92*).

In the study of substituted anthraquinones only ammonia–ammonium chloride buffers gave results that were comparable to potentiometric measurements. Phosphate and borate buffers formed complexes and stabilized semiquinones; tartrates and acetates interacted in only a few cases (*186*).

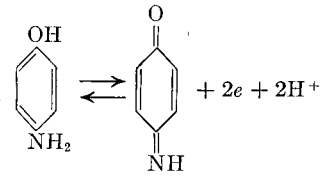
The method has been used to estimate aloins and aloe-emodin in Curaçao aloes. The latter, which is a hydroxyanthraquinone, is best determined spectrophotometrically, as fewer steps are involved (*185, 187*).

The reversibility of the catechol–*o*-benzoquinone, 4-methylcatechol–4-methyl-*o*-benzoquinone, and 2-naphthoquinone–1,2-dihydroxynaphthalene systems has been established at the dropping mercury electrode. The behavior of pyrogallol apparently is irreversible and difficult to interpret, as definite oxidation products could not be prepared (*50*). The only conditions reported to give reducible products were air oxidation in aqueous solution for 8 hours (*207*).

Sharply defined polarographic anodic waves can be obtained with a platinum microelectrode for hydroquinone, catechol, or ascorbic acid. Substances that undergo destructive oxidation, such as resorcinol, give curves with a sharp maximum peak followed by a continuous rise (*175*).

The polarographic method has been used to follow the decomposition of *o*-benzoquinone in water into catechol and an unknown compound which is neither 2-hydroxybenzoquinone nor purpurogallin (*51*), to investigate the nature of freshly prepared solutions of tannins (*24*), and to study the reaction of *o*-quinones with α-amino acids and with hydrogen peroxide. The product in the last reaction from its polarographic behavior is apparently a peroxidic *o*-benzoquinone (*51*).

p-Aminophenols give anodic waves at the dropping mercury electrode at more positive potentials than the corresponding hydroquinones. The values for the oxidation of 2,6-polymethylene-4-aminophenols, for example, are about 0.06 volt more positive than the value for the oxidation of the corresponding 2,6-polymethylenehydroquinones (*148*). The oxidation yields the quinoneimine and represents a reversible reaction;



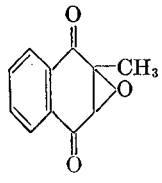
polarographically a value of +0.739 volt is found for E_0 of *p*-aminophenol, whereas potentiometrically a value of +0.733 volt is reported for the reduction of *p*-quinoneimine. This value is 0.028 volt more positive than that for hydroquinone.

The study of the system is not possible in all buffers, since the quinoneimine is hydrolyzed very easily to the quinone. The rate of this decomposition varies with the substituents present and is slow enough with the oxidation product of 4-amino-2-methyl-1-naphthol (vitamin K_5) so that the reaction can be followed polarographically.

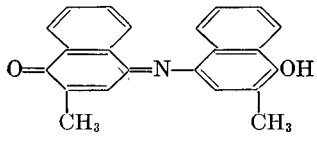
m-Aminophenol gives no reproducible wave and *o*-aminophenol gives in a borate buffer (pH = 9) a drawn-out anodic wave.

The polarographic method has demonstrated that the oxidation

products of vitamin K_5 formed by oxygen and by human red blood cells are 2-methyl-1,4-naphthoquinone and 2-methyl-1,4-naphthoquinone oxide (IV) and that the violet dye formed from this vitamin is an indophenol (V) (*108*).



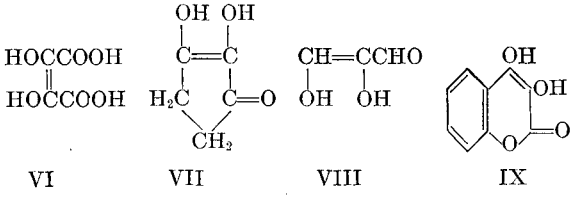
IV



V

The oxidation of *p*-phenylenediamines at the dropping mercury electrode is limited to only a few examples. Substitution of a platinum microelectrode, however, gives half-wave potentials which differ by not more than 3 to 7 mv. from those obtained by the dropping mercury electrode and increases the number of possibilities that can be studied (*103*). By this technique values for 55 different *p*-phenylenediamines were determined and found to be related to the development rate in photography and in part to the high allergenic potency of these compounds. Reversibility of this system is indicated by a two-electron slope for the curves but was not established definitely because the quinonediimines were too unstable to study (*10*).

Extensive work has been done on the oxidation of ene-diol systems to determine whether the irreversible behavior observed for ascorbic acid at the dropping mercury electrode is typical of this system. Dihydroxymaleic acid (VI) (*210*), reductic acid (VII) (*162*), reductone (VIII), and coumarindiol (IX) (*22*) all give irreversible anodic waves and behaviors resembling that of ascorbic acid. Only reductone (VIII) gave a cathodic wave that appeared close to the deposition of sodium ions. It has been suggested that the irreversibility of this system is caused by the hydration of the oxidation product (*22*).



VI VII VIII IX

Ascorbic acid gives an oxidation wave at a platinized platinum electrode (*124*).

In other reversible systems the polarographic method has been concerned mainly with the quantitative aspect. The method has been used to determine the amount of methylene blue adsorbed by charcoal (*95*) and the amount of alloxan in blood (*204*), and has shown that *p*-dimethylaminoazobenzene (dimethyl yellow) (*144*), Pontachrome Violet S W, and Pontachrome Blue Black R (*211*) give waves suitable for their determination.

IRREVERSIBLE SYSTEMS

Aldehydes. The polarographic behavior of acetaldehyde in various buffers has been verified and the degree of hydration calculated by comparing the diffusion current with that of an indicator wave (*48*, *49*). The half-wave potential of this compound differs very little from propionaldehyde and *n*-butyraldehyde, but by making use of a differential distribution between two immiscible solvents it has been possible to analyze binary mixtures and ternary mixtures of these compounds polarographically (*74*).

Addition of ammonia to an acetaldehyde solution produces a wave which is dependent upon the amount of ammonia present and which together with the aldehyde wave decreases on standing (*217*).

The polarographic determination of formaldehyde has been carried out in the presence of acetone and alkali using the cathode ray polarograph (*178*) and has been used to study the reaction between formaldehyde and urea (*40*, *41*), acetamide and benzamide (*42*).

The polarographic determination of acetaldehyde is used indirectly for determining lactic acid. The latter is oxidized to acetaldehyde by a mixture of potassium permanganate, phosphoric acid, and manganous sulfate (*47*).

Formaldehyde and acetaldehyde sulfoxylates, $RCHSO_2Na$, are
$$\begin{array}{c}\\ |\\ OH\end{array}$$
reported to be identifiable polarographically (*65*).

In the carbohydrate field the polarographic method has been used in two ways. Advantage has been taken of the effect of impurities (organic nonsugars) in refined sugars on suppressing the oxygen maximum in devising an empirical method for determining these substances (*202*). The determination has to be made under uniform conditions, as the effect is accentuated very easily by external conditions such as heat (*203*). Directly, the polarographic method has been used to determine fructose in various fruits without correcting for the glucose present (*212*).

The aldehyde group in the streptose unit of streptomycin must be responsible for the two reduction waves observed with streptomycin. This reduction makes the polarographic method a suitable one to follow the alkaline decomposition of streptomycin and mannosidostreptomycin, as the products are not reducible. The rate dependence upon pH is similar to that found polarographically for the rearrangement of α-hydroxyisobutyraldehyde to acetoin by alkali and is offered as evidence that the same general reaction is responsible for the rate-determining step in each example (*23*).

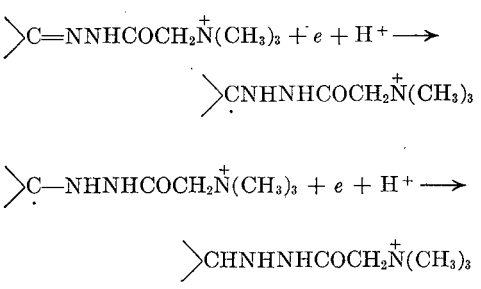
The polarographic behavior of the unsaturated aldehydes, citral, jasmine aldehyde, and citronellal, is reported in various media (*69*). Values are also given for benzaldehyde, *p*-dimethylaminobenzaldehyde, and cinnamaldehyde (*114*). Addition of ammonia is found to shift the benzaldehyde wave to more positive values by 0.210 volt (*217*).

The polarographic method has been used to determine benzaldehyde, anisaldehyde, cuminaldehyde, cinnamaldehyde, and citral in essential oils (*13*), and cuminaldehyde in cumin seed (*164*).

Ketones. The simple aliphatic ketones, acetone and cyclohexanone, are reduced in a 0.05 *N* tetraethylammonium iodide–75% dioxane solution at −2.46 and −2.45 volts (S.C.E.), respectively (*180*). No wave is observed in 0.1 *N* lithium hydroxide solution, but if ammonia or glycine is present at this pH a reduction wave occurs at −1.5 and −1.54 volts, respectively, for acetone (*217*). The height of the wave is influenced by the concentration of both the acetone and the ammonia and reaches a maximum height of 20% of what would be expected for the same concentration of pyruvic acid. The current is diffusion-controlled and reaches its maximum value after 15 seconds. It has been suggested that acetoneimine is responsible for this early reduction (*219*).

Waves at approximately the same point, −1.56 volts (S.C.E.), are obtained in a buffer of pH 8.2 for the Girard derivatives of acetone, methyl ethyl ketone, diethyl ketone, methyl *n*-decyl ketone, and di-*n*-octyl ketone. Cyclic ketone derivatives give values which vary between −1.50 and −1.63 volts, depending upon the size of the ring. The stability of the Girard derivative towards hydrolysis is influenced by the pH of the medium and is least for the cyclohexanone derivative (*147*). This instability explains the previous reported failure to reduce this compound and

substituted cyclohexanone derivatives (*214*). The polarographic data point to the following electrode reactions (*147*).



Ketones and aldehydes may likewise be determined indirectly by measuring their ability to decrease the wave of sulfur dioxide in a sodium bisulfite solution. This technique gives results which differ by about 2% from the values obtained by titrating the hydrogen chloride liberated in the oxime method (*189*).

Polarographic data are given for methylionone and pseudomethylionone (*69*).

The method has been used to determine carvone, pulegone, and diosphenol in essential oils (*12*), diosphenol in oleum bucco (*14*), and carvone in drugs (*15*).

In the steroid field the method has used the Girard derivatives to determine 3-ketosteroids in buffers with higher pH to prevent hydrolysis (*147*) and in combination with digitonin precipitation to estimate amounts of α- and β-17-ketosteroids (*25*).

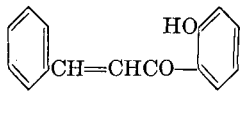
Steroids without reducible groups have been determined indirectly. Cholesterol has been estimated in both the free and bound form in blood serum by being precipitated with excess digitonin and determining the excess digitonin polarographically. This determination is dependent upon finding the amount of suppression of the cobalt maximum in an ammonia–ammonium chloride solution (*196*). Estradiol may be determined by converting it into estrone by means of a *Streptomyces* (*88*) or into a reducible nitroso compound. The latter reaction has also been used with estrone and estriol to give polarographically reducible compounds (*78, 87*).

Diacetyl has been reinvestigated and found to give only one wave at −0.67 volt in a tetramethylammonium bromide solution. The previously reported wave at −1.9 volts is apparently due to an impurity. Addition of ammonia gives a second wave at −0.53 volt which increases at the expense of the wave at −0.67 volt (*84*).

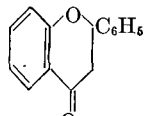
In the aromatic ketones series polarographic studies are reported for benzophenone, acetophenone, benzoylacetone (*112*), phenyl 2-naphthyl ketone (*4*), fluorenone, anthrone, benzophenone (*45*), and *p*-aminoacetophenone (*2*). The last compound, which reduces at −1.2 volts, gave the best yield of pinacol when large scale controlled electrolysis was carried out at −1.5 volts.

Compounds with more than one ketone group such as benzil (*67*) and ninhydrin (*206*) can be determined polarographically. The latter, owing to the occurrence of hydration and adsorption at the electrode, gives five waves in phosphate buffers and three waves in Britton buffers. It is best determined at a pH of 8.3 in buffers containing boric acid or borates.

In the aromatic unsaturated ketone series the effect of the substitution of hydroxyl groups in chalcones (X) upon the amount of bimolecular reduction and normal reduction at the dropping mercury electrode has been studied for 16 chalcones (X) (*68*).

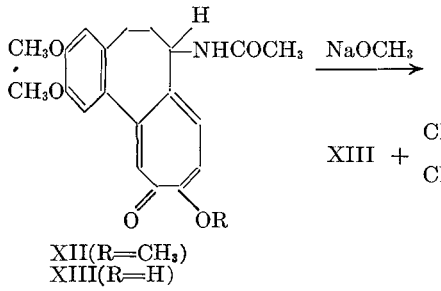


X

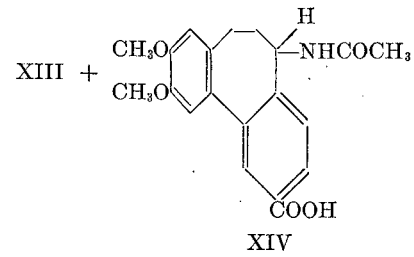


XI

The method has been used to follow the formation of chalcones and to distinguish between these compounds and the related flavanones (XI) (*169*), to show that the action of sodium methoxide upon colchicine (XII) produces colchiciene (XIII) and colchicic acid (XIV) (*160*)

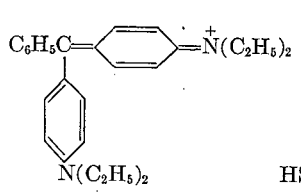


XII(R=CH_3)
XIII(R=H)

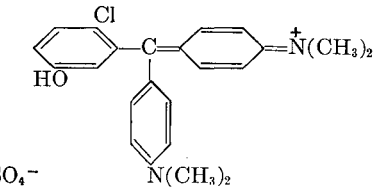


XIV

and that Brilliant Green (XV) and 2-chloro-5-hydroxy-4′, 4″-bis-dimethylaminotriphenylmethyl bisulfate (XVI) have similar structures (*123*).



XV



XVI

The polarographic method has been useful in determining ketones and aldehydes in a study of their relative strengths as oxidizing agents. Values are given for the reduction of 43 of these compounds (*1*).

Acids and Their Derivatives. Simple aliphatic acids give hydrogen waves at the dropping mercury electrode with half-wave potentials that become more negative with an increase in concentration of the acid (*116*); the ethyl esters give no waves (*180*). Polybasic acids, aromatic carboxylic acids, and sulfonic acids likewise give hydrogen waves, as do some of the substituted sulfanilamides having a first acid dissociation constant above 10^{-8}. Compounds having values below this, such as sulfidine, sulfanilamide, and boric acid, do not give a wave (*116*). This method can be used quantitatively (*115*).

Derivatives of benzoic acid differ from those of aliphatic acids and give reduction waves (*180*).

In the hydroxy acid series ascorbic acid or vitamin C gives an anodic wave which can be used to determine this compound in plants (*85*) using metaphosphoric acid, citric acid, or potassium citrate as an extracting medium (*140*). The oxidation product if prepared using air is not reducible unless ammonia is present (*217*).

Polymeric lactic acid may be determined quantitatively by using its effect upon the oxygen maximum (*99*).

Glucuronic acid, which is an aldehydohydroxy acid, is not reduced polarographically but upon standing gives reducible decomposition products (*97*).

Pyruvic acid, the simplest keto acid, in the presence of ammonia gives two waves, the first of which is dependent upon the concentration of the ammonia and is more positive than the second wave. A similar behavior is observed with glycine, alanine, cotarnine (*217*), histidine, and histamine (*216*). No effect occurs with dimethylamine, trimethylamine, tetramethylammonium chloride or hydroxide, di- and triethanolamine, and diphenylamine (*217*). A similar production of two waves is observed with sodium fluoride but not with the other halides (*121*).

The method may be used to detect pyruvic acid in a fermentation mixture (*157*).

Acetoacetic ester is reported not to be reducible at the dropping mercury electrode (*21*).

In the unsaturated acid series extensive work with fumaric and maleic acids and their ethyl esters in various buffers indicates that the reduction of the acids requires a buffering capacity of 0.9 *M* to obtain a regular behavior (*60*). Equations have been derived to account for the effect of ionic recombination on the polarographic limiting current caused by the reduction of the undissociated molecules or anions belonging to dibasic acids and have been verified by the experimental data obtained with maleic, fumaric, and citraconic acids (*82*).

The polarographic technique has been used to demonstrate the existence of unsaturation in 3,5-diiodo-4-(4′-hydroxyphenoxy)-cinnamic acid and 3,5-diiodo-4-(4′-hydroxy-3′,5′-diiodophenoxy)-cinnamic acid (*208*) and to show that β,γ-angelica lactone and α,β-angelica lactone form a reducible peroxide with air. Only α,β-angelica lactone is reducible at the dropping mercury electrode (*105*).

Organic Halogen Compounds. A wide variety of organic halogen compounds has been studied polarographically. From a study of alkyl halides, aryl halides, and polyhalogen and unsaturated halogen compounds the following observations have been made.

1. Iodides reduce more easily than bromides and these more easily than chlorides.
2. The more halogens there are on a carbon atom the more positive is the potential and the greater is the number of waves.
3. Allylic halides are more easily reduced than vinyl halides. Controlled large scale electrolysis indicates that the unsaturation is not affected.
4. The longer the aliphatic chain the more difficult the reduction.
5. The ease of reduction of a halogen attached to an aromatic ring is similar to that of a halogen attached to a large alkyl group.
6. The half-wave potential is independent of pH.

In the majority of cases the waves represent reduction of the halide to the hydrocarbon.

$$RX + 2e + H^+ \longrightarrow RH + X^-$$

This mechanism has been confirmed by controlled electrolysis on a large scale for methyl iodide, ethyl bromide, α-bromonaphthalene, allyl bromide, 1,2-diiodoethene, and diiodoacetylene.

Vicinal dihalogen compounds are exceptions in that they give intermediates which form olefins. Thus, ethylene bromide gives 80% ethylene and 20% ethane and 2,3-dibromobutane gives butylene (*180*).

Factors such as ionic strength, alcohol content, and the nature of the cation of the supporting electrolyte have been found to be important in the reduction of aromatic iodides (*71*).

Substitution of a fritted-glass disk electrode for the dropping mercury electrode gives similar results with organic halogen compounds (*137*).

Introduction of another functional group into the organic halide molecule changes the behavior only with respect to the effect of pH upon the half-wave potential. In the α-halogenated acid series, for example, the half-wave potential is independent of pH in regions where only one species of the acid is present. In the intermediate region the half-wave potential becomes more negative with an increase in pH (*155*). Values are reported for α-bromoacetic (*57*, *156*), α-bromopropionic (*155*), α-bromobutyric (*56*), dibromoacetic, tribromoacetic, iodoacetic (*57*), dichloroacetic, and trichloroacetic acids. Chloroacetic acid gives no reduction in the range +0.4 to −2.00 volts (*59*).

The reduction of *meso*-α,α'-dibromosuccinic acid parallels the behavior of the simple 1,2-dibromo compounds and forms fumaric acid by a trans elimination (*153*).

Results are also reported for bromoacetic acid (*136*) and chloroacetamide at the fritted-glass disk electrode (*137*), and for the iodobenzoic acids at the dropping mercury electrode. The mechanism in the latter series has been checked for *p*-iodobenzoic acid by a large scale electrolysis at controlled potentials (*71*).

A similar dependence of half-wave potential upon pH has been observed with the iodoanilines (*71*) and halogenated acetaldehydes (*63*, *106*). The behavior of the latter class is complicated by hydration of the aldehyde group. Reduction of the halogens is likewise observed for the acetals of these compounds.

The polarographic method has been used to determine chloroform and carbon tetrachloride separately and in mixtures of the two (*110*), carbon tetrachloride in mixtures with tetrachloroethylene, and carbon tetrachloride and chloroform in mixtures with methylene chloride and methyl chloride (*180*).

The isomers of hexachlorocyclohexane have been intensely studied polarographically because of the importance of the gamma isomer as an insecticide. The reduction wave obtained for the γ- isomer and α- isomer involves six electrons and represents the formation of benzene. This mechanism has been verified on a large scale (*168*). The reduction can be limited to the γ-isomer by using either 1% potassium iodide (*94*) or 0.1 *N* ammonium chloride as the electrolyte (*215*) and will give good accuracy in a quantitative determination if the temperature is held constant (*132*) and a correction is made for the heptachlorocyclohexane, since this compound changes the base line (*134*). Octachlorocyclohexane if present will also give a wave (*139*). Location of the γ-isomer wave can be facilitated by adding zinc ions to the electrolyte; the zinc wave will come directly before the start of the wave for the γ- isomer (*30*).

The polarographic method has been used to show that a reaction occurs between the γ-isomer and cysteine (*198*), to follow the dehydrochlorination of the various isomers in kinetic studies (*98*, *133*), and to determine the γ-isomer in commercial insecticides containing the other isomers, talcum powder, mercuric compounds (*76*), or DDT. The last compound gives a wave at a more positive value which represents all the isomers of DDT (*197*). Better accuracy is reported for the polarographic determination of the γ-isomer than for the infrared method (*193*).

The isomers of hexachlorocyclohexane suppress the oxygen maximum in the following order: γ, β, δ, α, ϵ (*34*).

Polarographically dichloroacetic acid and trichloroacetic acid can be determined in mixtures (*58*).

In the aromatic series polarographic investigations have mainly concerned themselves with the determination of thyroxine and related compounds. Out of 23 related substances only 3,5-diiodo-4-(4′-methoxyphenoxy)benzoic acid and 3,5-diiodothyronine interfere with the determination of thyroxine. 3,5-Diiodotyrosine interferes only if its molar ratio is greater than 10 (*19*).

This method has been used to determine thyroxine in Ardein (ground nut protein), thyroid powders, and casein (*174*), and to show that cleavage of the diphenyl ether structure of 5-(3′,5′-diiodo-4′-*p*-methoxyphenoxybenzyl)hydantoin occurs in treatment with 57% hydriodic acid (*18*).

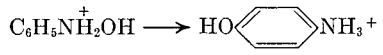
Nitro Compounds. A variety of aliphatic nitro compounds have been studied polarographically. Values are reported for nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane in aqueous buffers (*181*). The presence of hydroxyl groups does not change the mode of reduction of the nitro group in 3-nitro-2-butanol, 2-nitro-1-butanol, 1-nitro-2-butanol, 2-methyl-1-nitro-2-propanol, and its di- and trihydroxy derivatives but made it easier than reduction of the hydrocarbon. With all compounds a four-electron reduction to the hydroxylamine is involved (*170*). Conversion of 2-nitro-1-butanol into an ether or ester made it more easy to reduce polarographically. The formyl and acetyl derivatives' behavior was complicated by the loss of formic and acetic acids, respectively, and formation of the 2-nitro-1-butene which hydrated to 2-nitro-1-butanol (*171*). This transformation of the acetate can be followed polarographically (*172*).

Tetranitromethane gives polarographic waves in a variety of buffers. The wave at pH 12 is suitable for concentration deter-

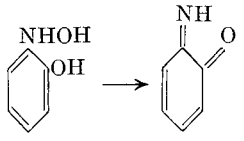
mination but overlaps with that of dinitrobenzene and trinitrobenzene if these are present. The tetranitromethane can be removed from such solutions by adding methanol and vacuum distilling at 70° C. (*44*).

The method has been used to determine nitromethane in air using an evacuated Winchester to obtain a sample (*213*).

In the aromatic series more information has been found about the reduction of nitro groups. By oscillographic measurements nitrobenzene is found to reduce four times more quickly than nitromethane (*90*). The second wave has been found to be partially kinetically controlled and must involve in addition to the reduction of phenylhyldroxylamine to aniline the following rearrangement (*182*).



Previous results on *o*-nitrophenol could not be verified. The compound gives a four-electron reduction at pH 6 and a six-electron reduction in more acid or alkaline region. The reason for this behavior is that the resulting hydroxylamine can form a quinoneimine which is reduced further to the aminophenol (*182*).



A similar process must be involved in the reduction of *p*-nitroaniline, as a six-electron wave is obtained at all pH values studied (*173*).

Polarographic behaviors of *p*-nitrobenzoic acid (*62*), *o*-, *m*-, *p*-nitrobenzaldehydes (*118*), *p*-nitrophenol (*143*), 4,4′-dinitrodiphenyl ether, 4-nitrodiphenyl ether, and 4-nitro-4′-aminodiphenyl ether (*130*) are reported. The addition of alcohol has been found to shift the half-wave potentials to more negative values.

The reduction of nitrobenzene has also been studied at copper, silver, and amalgam spherical electrodes in 0.1 *N* potassium chloride (*124*).

The polarographic method has been used to determine nitrobenzene in small amounts in aniline (*194*), *m*-dinitrobenzene in nitrobenzene (*195*) and blood serum and plasma (*154*), nitroxylene and dinitroxylenes in nitroxylene feeds and resulting xylidines (*79*), picric acid in the presence of phenol (*135*), chloromycetin in broths, concentrates, and solids (*86*), trinitrobenzene and dinitrobenzene in the presence of each other (*43*, *44*), and parathion [p-$NO_2C_6H_4OPS(OC_2H_5)_2$] in dusts and wettable powders. In the last example *p*-nitrophenol does not interfere but the oxygen analog gives waves at the same point (*20*).

The method has also been used to demonstrate that the nitro group in 5-nitro-2-furfuraldehyde semicarbazone is more easily reduced than either the semicarbazone group, or the nitro group in nitrobenzene and 5-nitropyridine (*199*), and that the nitro group is chelated in 4-nitrobenzimidazole (*150*).

Using a streaming mercury electrode and "derivative" curves it is possible to differentiate between *o*-, *m*-, and *p*-nitrophenols in the presence of nitrobenzene (*89*).

Nitroso Compounds. The nitrosobenzene–*N*-phenylhydroxylamine system is reversible at the dropping mercury electrode. The reduction wave of nitrosobenzene involves two electrons and is followed in acid solution by a further reduction of the phenylhydroxylamine to aniline (*176*). This second step has been verified using phenylhydroxylamine (*182*).

Reduction of nitrosoamines is possible in acid solution and is the basis for the analysis of dimethylamine in the presence of methylamine and trimethylamine. Nitromethane, which is formed as a by-product in the reaction of nitrous acid on methylamine, is removed by sodium hydrosulfite (*61*).

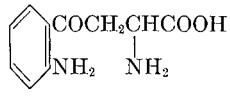
Nitroso R salt is reported to be reduced polarographically (*73*).

Amino Acids and Their Derivatives. Amino acids and their derivatives do not give reduction waves unless some reducible group is present. They will give a hydrogen wave, however, if the dissociation constant is greater than 10^{-8}. This wave has served as a basis of estimation in the aromatic amino acid series for anthranilic, sulfanilic, and naphthionic acids (*115*).

Amino acids may be determined also indirectly by forming a metal complex and determining this substance polarographically. The copper complex has been used most frequently (*102*), but the nickel complex may be likewise suitable (*145*).

This method has been used to determine amino acids separated by paper chromatography (*129*) and to determine the amount of ethylenediaminetetraacetic acid in the commercial product (*66*).

The polarographic behavior of kynurenine resembles that of acetophenone, *o*-aminobenzaldehyde, and lobeline and favors structure (XVII) for this compound (*159*).



XVII

Certain sulfonamides such as sulfathiazole, sulfadiazine, 3-sulfapyridine, and sulfacetamide give hydrogen waves in 0.1 *N* tetramethylammonium iodide solution (*113*). Sulfanilamide does not give a wave up to −2.3 volts but is surface active and lowers the oxygen maximum to varying degrees. A similar effect has been observed with *p*-aminobenzoic acid (*205*) and sulfanilic acid (*165*).

The tripeptide glutathione (glutamylcysteinylglycine) is reported to give three anodic waves in alkaline solutions, the third of which interferes with the determination of ascorbic acid. The concentration of the former in fruits is not high enough to affect the ascorbic acid determination (*39*).

The polarographic method has demonstrated the presence of albumins or globulins and peptones in port wine (*3*).

Diazonium Salts. Benzenediazonium chloride yields two waves in buffered solutions containing tetramethylammonium chloride. The first wave is independent of pH and represents the following electrode reaction.

$$C_6H_5N_2^+ + e \longrightarrow C_6H_5\cdot + N_2$$

This mechanism has been verified by coulometric analysis and the isolation of phenylmercuric chloride and diphenylmercury in a large scale electrolysis at controlled potential. The second wave, which is about four times as high, is pH-dependent and probably represents the following electrode reaction:

$$C_6H_5N_2^+ + 4e + 3H^+ \longrightarrow C_6H_5NHNH_2$$

Coulometric analysis and large scale electrolysis, however, give similar results to those observed for the first wave. One explanation for this discrepancy is that the stirring in the latter removes the intermediate from the electrode surface and prevents further reduction (*5*). Substituted diazonium salts behave similarly, with the exception that if acid groups are present the first wave varies with pH (*5*, *54*).

The polarographic reduction of diazonium salts is the basis for the amperometric titration of couplers in the dye industry (*55*) and of pharmaceutical compounds containing phenolic and amino groups (*101*), and has been used to follow diazotization rates and decomposition rates of diazonium salts. The cathode ray polarograph is especially useful for reactions of this type, for which the rates are very fast (*178*).

Unsaturated Hydrocarbons. Aliphatic unsaturated hydro-

carbons such as butadiene, allene, ethynylacetylene, vinylacetylene, and divinylacetylene are reducible polarographically, while simple ethylenes and acetylenes are not (*180*).

In the aromatic series the effect of substituents in the ring and on the α- and β-carbon atoms of stilbene upon the ease of reduction has been studied (*75*). Stilbestrol under these circumstances is not reduced but may be determined by its suppression of the oxygen maximum (*11*).

Styrene has been found to give a satisfactory curve in a 75% alcohol solution containing 0.2 *M* tetrabutylammonium iodide (*190*) and can be determined in crude benzene fractions with a maximum error of 5.9% (*191*).

A straight-line relationship has been obtained 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 (*127*) and verifies the previously postulated mechanism for the reduction of these compounds (*122*). Including the solvation energy of the ions in the calculations does not change the relationship (*125*).

The polarographic method has been used to determine carotene in plants (*91*).

Peroxides. Single polarographic waves have been obtained with dibenzoyl peroxide, cumene hydroperoxide (*72*), and ascaridol (*12*) and are suitable for their determinations. Methyl methacrylate peroxide, vinyl acetate peroxide, and styrene peroxide give two waves, the second of which resembles that for *tert*-butyl peroxide. Electrolytic reduction of the styrene peroxide gave phenylglycol and indicated that these peroxides are polymers of the monomer and oxygen with a hydroperoxide (HOO—) end group (*8*).

Sulfur Compounds. Dialkyl disulfides and diaryl disulfides are reduced at the dropping mercury electrode in a two-electron step.

$$R—S—S—R + 2H^+ + 2e \longrightarrow 2RSH$$

The method can be used to determine these compounds alone or in the presence of sulfur (*70*). The presence of groups other than carbon does not seem to change the mode of reduction in cysteine sulfonate (*111*)

$$R—SSO_3^- + 2e \longrightarrow RS^- + SO_3^{--}$$

and bis-(diethylthiocarbamyl)disulfide (*77*); both give waves involving two electrons. In the second example an adsorption wave is observed.

$$(C_2H_5)_2NC(=S)—S—S—C(=S)—N(C_2H_5)_2 + 2e \longrightarrow 2(C_2H_5)_2N—C(=S)—S^-$$

The method has been used to study the reaction of cystine and dithioglycolic acid with sulfite (*188*).

$$R—S—S—R + SO_3^{--} \rightleftharpoons RS^- + RSSO_3^-$$

2-Thiohydantoins give anodic curves at the dropping mercury electrode but no catalytic hydrogen waves in ammoniacal cobalt solutions (*32*). The latter phenomenon is shown by degradation products of penicillin and can be used to determine pure penicillin if this antibiotic is inactivated first with alkali. The results agree within 10% of the biological assay (*33*).

p-Aminophenylthiocyanide and *p*-dimethylaminophenylthiocyanide are reported to undergo a six-electron reduction at the dropping mercury electrode. As the wave height decreases with an increase in pH, the possibility of a catalytic wave cannot be discounted (*167*).

Arsonic Acids. Arsonic acids give a wave in acid solutions of a height which points to the following electrode reaction.

$$ArAsO_3H_2 + 6H^+ + 6e \longrightarrow ArAsH_2 + 3H_2O$$

By making use of the reduction of the nitro group in *m*-nitrophenyl arsonic acid it is possible to use this compound in amperometric titrations of uranyl, thorium, zirconium, and stannic tin (*109*).

Organometallic Compounds. Phenylmercuric salts, C_6H_5HgX, give two waves at the dropping mercury electrode, the half-wave potentials of which are independent of the anion (X) used. The first wave represents the following reaction:

$$RHgX + e \longrightarrow RHg + X^-$$

while the second involves the following change:

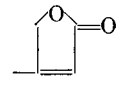
$$RHg + H^+ + e = RH + Hg$$

Large scale electrolysis gave diphenyl mercury, a disproportionation product of diphenyl dimercury. Merthiolate, *p*-chloromercuribenzoic acid, and Salygan behave similarly (*9*). In the aliphatic series the behavior is reported to be different; the anion as well as the radical affects the half-wave potentials observed (*35*).

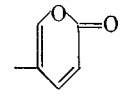
By using the second wave it is possible to determine Merthiolate in antiseptics and vaccines but not in whole blood or in the presence of antimony compounds (*141*).

The behavior of other organometallic compounds has been studied and is reported for dichlorodiethyltin (*151*), trialkyltin halides (*38*), trialkyllead bromides (*36*), and dialkylthallium bromides (*37*). Tetraethyllead is not reducible polarographically but can be determined indirectly by decomposing the compound with nitric acid (*107*) or with hydrochloric acid (*81, 138*) and determining the lead.

Oxygen Heterocyclic Compounds. Heart poisons having the γ-lactone structure (XVIII) are reducible polarographically only in quaternary ammonium hydroxide or halide solution. Compounds with the pyrone structure (XIX) reduce more easily by 0.5 volt and can be determined in ammonium chloride, potassium chloride, potassium hydroxide, or lithium chloride solution. The substances give waves of two electrons and can be determined in the presence of each other (*131, 163*). The method was suitable for determining these substances in squill and various drugs (*163*) and has been used to determine digitoxin in blood (*93*).

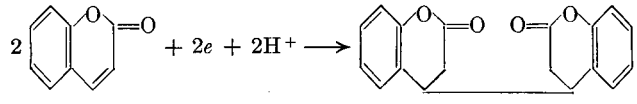


XVIII



XIX

Coumarin (XX) gives a single wave which is independent of pH and represents a one-electron reduction to the dihydrodicoumarin (XXI).



XX XXI

This mechanism has been verified on a large scale. Analysis is best carried out at pH 6.8, because beyond this value the lactone ring starts to open and form coumarinic acid with a corresponding decrease in diffusion current. Above pH 11.2, for example, very little coumarin is present. Substituted coumarins behave in a similar fashion (*26, 83*).

Flavones as a rule give two reduction waves which may coa-

lesce if hydroxyl groups or derivatives of these are present. Each wave involves one electron and represents reduction to the pinacol and alcohol, respectively (*68*).

Flavanones give only one reduction wave involving two electrons. Groups when substituted in the 5- and 7-positions will affect the half-wave potentials (*68*).

Polarographic data are given for the naturally occurring flavones, rutin, quercetin, and morin (*27*), and the furochromones, khellin, visnagin, and khellol glucoside. Differentiation qualitatively of khellin and visnagin is not possible (*6*). Quantitative estimation of khellin and visnagin is equivalent, however, in accuracy to the ultraviolet determination but is less convenient to carry out (*53*).

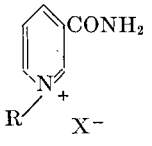
The fluorescein dyes, Uranin, Eosin, Erythrosin, and Rose Bengal are reducible at the dropping mercury electrode (*64*), but the closely related Mercurochrome is reported not to reduce (*66*).

Nitrogen Heterocyclic Compounds. Pyrroles substituted with alkyl groups in the 1-, 2-, and 3- positions are not reduced polarographically (*16*). Pyrrolesulfonic acids are likewise inert but are reported to be oxidized at the dropping mercury electrode. As these anodic waves are reported in 0.5 *N* potassium chloride and occur from 0.015 to 0.052 volt, the actual process occurring at the electrode is questioned (*200*).

The polarographic behavior of isatin is complicated because of the possibility of ring opening and subsequent formation of three reducible species (*192*). The method can be used, however, to determine isatin in acid or alkaline medium (*119*), and has been employed to study the kinetics of the formation of isatinic acid from isatin (*120*).

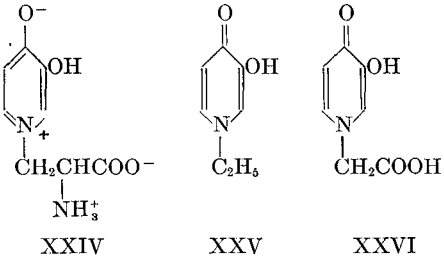
Polarographic studies are also reported for dihydroxyindole (the reduction product of isatin), indigocarmine (*119*), and phthalimide (*117*).

In the pyridine series pyridinium salts related to one of the components of codehydrase have been studied polarographically. Values are reported for pyridinium methobromide, trigonelline, isonicotinamide methobromide, 1-tetraacetylglucosido-3-carbamylpyridinium bromide, cozymase, nicotinamide methobromide (*179*), and related pyridinium chlorides, bromides, and iodides (XXIII) in which the alkyl group was varied from methyl through butyl (*31*).



XXIII

The polarographic method indicates that mimosine has structure XXIV, as waves resembling those of pyridones XXV and XXVI are obtained (*17*)



XXIV XXV XXVI

and has been used to follow the hydrolysis of nicotinamide (*100*).

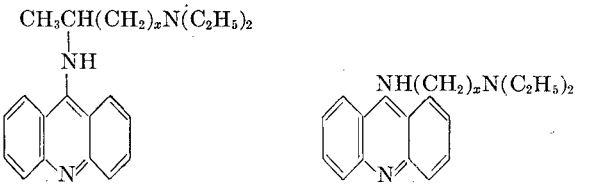
In the quinoline series polarographic values are reported for 8-quinolinol (*96*) and cinchoninic acid (quinoline-4-carboxylic acid) (*29*).

The polarographic reduction of quinaldinic acid (*183*) and of quinoline-8-carboxylic acid (*184*) is the basis for the amperometric titration of copper. The former may also be used for the determination of zinc.

Molecular orbital calculations for the introduction of a methyl group into a pyridine nucleus predict a shift of −0.030 volt. The experimentally obtained half-wave potentials for 2-methyl- and 2,6-dimethylquinolinium methiodides differ by −0.039 volt (*126*). The significance of this agreement is questioned, since the example cited illustrates the introduction of a methyl group into a benzenoid nucleus and not into a pyridine ring.

A very careful polarographic study of acridine indicates that the complex behavior is due to adsorption of the acridinium ion, because the anomalies are worse in acid solution. The complex behavior disappears in solutions containing 50% or more of alcohol and is replaced by two one-electron reduction steps. Methylacridinium salts give similar adsorption phenomena in both acidic and basic medium which are not eliminated by alcohol (*104*).

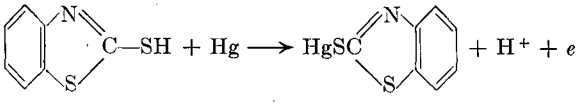
Substituted acridines related to Mepacrine (XXVII) ($x = 3$)



XXVII
x = 1–4 x = 2–7

give behaviors similar to acridine but show no definite correlation between antimalarial activity and the reduction potential observed (*80*).

Mercaptobenzothiazole (XXVIII) gives a cathodic wave only in the pH range 2.5 to 7 and an anodic wave in the range 1 to 13. Large scale electrolysis at +0.1 volt gave a white precipitate and very little mercuric ion in solution and suggested the following reaction for the anodic wave (*166*).



XXVIII

The polarographic behavior of pterins is similar to that for pteroylglutamic acid (vitamin B_c) and is good evidence for the structure of the latter (*28*).

The method is suitable for the quantitative estimation of vitamin B_c (*52*). Tablet constituents do not interfere but ferrous sulfate, if present, will give high results (*128*).

Barbituric acid is not reducible polarographically in 0.2 *M* tetraethylammonium bromide (*52*).

The polarographic method has been used to determine berberine, cotarnine, and hydrastinine in pharmaceutical preparations (*158*), colchicine in seed extracts or tinctures (*161*), and strychnine in viscera (*201*).

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Acid-Base Titrations in Nonaqueous Solvents

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ACID-base titrations in nonaqueous media possess the accuracy, speed, and simplicity required for good analytical methods. The equipment is inexpensive and available in any analytical laboratory equipped to do aqueous titrations. The analytical possibilities are comparable to those of aqueous titrimetry (*56*). Recent applications of titrations in nonaqueous solvents have reduced greatly the cost of control and specification analyses (*35*).

This subject is being reviewed for the first time. Unfortunately there is no index to acid-base titrations in nonaqueous solvents. The only means of making a survey of the literature at the present time is to consult recent articles and their references. Many of the review articles dealing with the theoretical aspects have extensive bibliographies.

The bibliography at the end of this article is necessarily incomplete because of the difficulty in locating publications in this field. Many of the earlier papers have been included because they contain significant historical material.

E. J. Crane, editor of *Chemical Abstracts*, is studying suitable means for indexing this field. A bibliography of literature pertaining to acid-base titrations in nonaqueous solvents is being compiled by Marion M. Davis of the National Bureau of Standards. The references given in this review may serve as an interim source of background material for persons interested in this field.

HISTORICAL

The concept of electrolytic dissociation has dominated the field of acid-base titrations for over half a century. At the turn of the century and until 1926 the theory was almost universally accepted. It was realized by some that the theory was limited mainly to aqueous media and could not be applied to neutralization reactions in other solvents. In 1902 Kahlenberg (*40*) pointed out several "ionic type" reactions that took place in benzene, a solvent in which ions did not exist according to the electrolytic dissociation theory. The following year Vorlander (*74*) reported the titration of aniline with hydrogen chloride in a benzene system using *p*-dimethylaminoazobenzene (methyl yellow) as the indicator. He was studying color changes and structure of dyes and did not consider the analytical significance of his experiments.

Folin and Wentworth (*19*), in 1910, published the first analytical method of titrating in nonaqueous media. They found that the higher fatty acids could be titrated with sodium alcoholate to a sharp end point in chloroform, carbon tetrachloride, benzene, or toluene. They believed their method represented a new departure in alkalimetry. Two years later Folin and Flanders (*18*) extracted hippuric acid from urine with chloroform and titrated it with sodium ethylate. The same years they (*17*) questioned the validity of the theory of ionization when applied to all solvent systems.

In 1923 Hantzsch (*30*) presented a study of the nature of acids that showed a departure from the prevailing theory. In the same year Brønsted (*7*) published the preliminary concept of his theory of acids and bases. Early the following year Lowry (*53*) independently published essentially the same theory.

The first recognition of titrations in nonaqueous media appears to be an electrometric procedure for the determination of acidity in oils published in the *Proceedings of the American Society for Testing Materials* in 1925. In the following years several modifications of this procedure were reported (*10*, *15*, *65*, *68*, *69*). In 1927 Hall and Conant (*25*) and Conant and Hall (*11*) published their studies on "super acids." LaMer and Downs (*49*), in 1931, were probably the first to titrate acids and bases potentiometrically in an aprotic solvent. Two years later Lavine and Toennies (*50*) used the two color changes of thymol blue to distinguish between strong and weak acids in chloroform. Vorlander (*75*), in 1934, and Vorlander, Fischer, and Felicitas (*76*), in 1933, studied the titration of amines and alkaloids in chloroform. They proposed the name "aminometry" for the titration of aminelike substances in nonaqueous solvents. The procedure of Nadeau and Branchen (*59*), in 1935, for the determination of amino acids in acetic acid solutions was the first method of acid-base titration in nonaqueous systems to find wide acceptance.

THEORETICAL

Stoichiometric reactions in nonaqueous media take place in solvents that may or may not take part in the reaction. The solvents are divided into two classes.

Aprotic Solvents. These solvents are inert and are not believed to take part in neutralization reactions. They have a zero or very small dipole and do not readily form complexes. Most of the saturated and benzene-type hydrocarbons and some of the halogenated hydrocarbons, such as carbon tetrachloride and chloroform, belong to this group.

Amphiprotic Solvents. These solvents have an appreciable dipole moment, or have groups with dipoles such as *p*-dioxane. They are believed to take part in neutralization reactions in a manner similar to that of water. Lower fatty acids, alcohols, and amines belong to this class.

There are three well-known theories that may be used to explain neutralization reactions in any solvent system.

Hydrogen Bond Theory. The hydrogen bond, or hydrogen bridge, theory apparently was propounded by Moore (*57*) in 1907. A discussion of the theory is given by Pauling (*64*). While the literature relating to this theory is voluminous, it is not the one used most frequently to explain the type of reactions generally thought of as neutralization.

Lewis Theory. Lewis proposed his theory of acids and bases (*52*) in 1923. According to this theory, a base is an electron donor and an acid is an electron acceptor. Neutralization reactions take place because of a molecule of more stable electronic configuration results from the sharing of one or more pairs of electrons. Lewis acids and bases include the commonly accepted ones plus such compounds as aluminum chloride, stannic chloride, boron chloride, and copper(II). A discussion of the Lewis theory, as well as other theories relating to neutralization, was published by Luder and Zuffanti (*55*).

Brønsted Theory. This theory was first published in 1923 (*7*) and later was amplified and clarified (*5*, *6*). Brønsted subsequently discussed the particular application of his theory to amphiprotic solvents (*8*).

According to this theory an acid is a proton donor and a base a proton acceptor; thus

$$\underset{\text{acid}}{A} \rightleftharpoons \underset{\text{base}}{B} + \underset{\text{proton}}{H^+}$$

or using a familiar acid

$$\underset{\text{acid}}{HCl} \rightleftharpoons \underset{\text{base}}{Cl^-} + \underset{\text{proton}}{H^+}$$

It is apparent that when an acid loses a proton it becomes a base. Conversely, a base accepting a proton becomes an acid.

An acid or a base may be an ion or an electrically neutral molecule—for example:

$$\underset{\text{acid}}{H_2O} \rightleftharpoons H^+ + \underset{\text{base}}{^-OH}$$

$$\underset{\text{acid}}{HC_2H_3O_2} \rightleftharpoons H^+ + \underset{\text{base}}{C_2H_3O_2}$$

$$\underset{\text{acid}}{NH_4^+} \rightleftharpoons H^+ + \underset{\text{base}}{NH_3}$$

$$\underset{\text{base}}{H_2O} + H^+ \rightleftharpoons \underset{\text{acid}}{H_3O^+}$$

Water acts both as an acid and a base and the equilibrium may be represented as

$$\underset{\text{acid}}{H_2O} + \underset{\text{base}}{H_2O} \rightleftharpoons \underset{\text{acid}}{H_3O^+} + \underset{\text{base}}{^-OH}$$

An acid dissolved in water or acetic acid would reach the following equilibrium:

$$\underset{\text{acid}}{HClO_4} + \underset{\text{base}}{H_2O} \rightleftharpoons \underset{\text{acid}}{H_3O^+} + \underset{\text{base}}{^-ClO_4}$$

$$HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + {}^-C_2H_3O_2$$

$$HClO_4 + HC_2H_3O_2 \rightleftharpoons H_2C_2H_3O_2^+ + {}^-ClO_4$$

The Brønsted theory is believed by many to be compatible with both the hydrogen bond and Lewis theories. The acid and base reactions are usually explained on the basis of either Brønsted or the Lewis theory. The Brønsted and Lewis bases are the same. The difference between the two theories is that Lewis includes as acids, ions or molecules that form covalent bonds with a base such as boron trichloride, sulfur trioxide, and silver iodide, and the reaction product is not necessarily a salt. Brønsted acids are limited to ions or molecules that donate a proton, or hydrogen ion. Lewis acknowledged the usefulness of the Brønsted acids as a subclass and suggested the name "hydrogen acids" or "H-acids."

There has been considerable discussion concerning the differences and likenesses of these two theories. Luder (*54*) has shown that proton donors must be included with electron acceptors. Kolthoff (*44*) suggested that the Brønsted definition remain unchanged and that the larger group of acids be designated "Lewis acids" or "proto acids." Davis and Schumann (*13*) suggested it is more logical to consider the Brønsted acids as a special subclass. Bartlett and Dauben (*2*) concluded that Lewis and Brønsted acidity does not run completely parallel and believed that one class of acids cannot be completely absorbed in the other. Ferreira (*16*) stated that the two processes are not thermodynamically equivalent and that Brønsted acidity cannot be included in the Lewis acidity. He concluded that the Lewis definition includes the Brønsted acids but the two kinds must be studied separately.

Practically all acid-base titrations in nonaqueous solvents developed to date have been concerned with Brønsted or H-acids. The nonhydrogen acids have not been used as analytical reagents, nor have they been titrated with bases (except *17*, footnote) mainly because indicators, potentiometric systems, or other means have not been found for indicating the equivalent point. Another factor that has deterred the development of their use is given by Davis and Schumann (*13*): "the fundamental principles governing acid-base reactions in various types of organic solvents are less understood than the principles governing these reactions in aqueous media and are considerably less familiar to the average chemist."

The nature of the H-acids has been extensively studied by Hantzsch (*29*, *30*) and Hantzsch and Voight (*31*). Bell (*3*) has discussed the use of the terms "acid" and "base."

The idea of "super acids" was advanced by Hall and Conant (*25*) and the strength of acids and bases was studied by Conant, Hall, and Werner (*11*, *12*, *25*, *26*) in their studies in acetic acid. Hall has discussed this work and its significance (*24*). Hammett and Dietz (*28*) believed that formic acid is more deserving of the term "super acid" than is acetic acid. There are too many difficulties encountered in using formic acid as a solvent. Among them is its instability as a compound. Palit (*60*) proposed the use of a glycol-hydrocarbon solvent and postulated that a glycol increases the strength of an acid.

The information on the strength of acids and bases in organic solvents is meager. Present knowledge indicates that the strength will have to be determined for each acid and base for each amphiprotic solvent used. Izmailov (*36*) has reviewed the available information and arrived at the same conclusion. He concluded that the variation of the strength of an acid or base from solvent to solvent is determined by the basicity of the solvent. The relative acidity of two acids will vary from solvent to solvent, and the variation of the ratio of their acidity will be greater the more different are the acids. Hammett and Deyrup (*27*) concluded that the relative strength of two bases of the same charge type is independent of the medium in which they are compared. The relative strength of some acids and bases has been determined in a few solvents (*2*, *12*, *25*, *26*, *37*, *79*).

SOLVENTS

A variety of organic liquids have been used as solvents for acid-base determination. Solvents, as such, have not received very much consideration or study. Hall and Conant (*25*) and Conant, Hall, and Werner (*11*, *12*, *26*) investigated acetic acid as a solvent. No other solvent has received so extensive a study. Moss, Elliott, and Hall (*58*) made a study in ethylenediamine. They concluded that any outstanding progress in the field will probably depend first on a drastic departure from conventional solvent titrant combinations.

Palit (*60*) proposed a G-H solvent for the estimation of weak acids: ". . . G stands for any glycol type solvent and H represents any solvent for hydrocarbons, such as hydrocarbons themselves, alcohols, chlorinated hydrocarbons, etc." This solvent was developed during Palit's (*61*, *62*) and Palit and McBain's (*63*) study of solvents for soaps.

Ruehle (*66*) studied potentiometric titrations of acids in 2-methoxyethanol (methyl Cellosolve), acetone–butyl alcohol mixtures, anisole (methyl phenyl ether) and *p*-dioxane–*n*-butyl alcohol mixtures.

Gordy (*23*) determined the basicity of 26 solvents by determining the shift in the infrared OD band when the compound was mixed with CH_3OD. The basicities can be quantitatively estimated relative to benzene, equal to zero.

The choice of a solvent depends on the nature of the substance to be determined. The solubility, the reaction product with the titrant, and a means of determining the equivalence point of the reaction are important considerations. 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. Wilson (*77*) found that the indicator end point was sharper in acetic acid–hydrocarbon mixture than in acetic acid alone. Palit (*60*) found mixed solvents preferable. Fritz used a wide variety of solvents for his studies, and he and Lisicki (*22*) found that for the titration of most carboxylic acids and other moderately acidic compounds benzene-methanol was the preferred solvent.

Most analytical methods have been developed using acetic acid as the solvent. (The adjective "glacial" has been omitted in this review. Acetic acid refers only to glacial or anhydrous acetic acid.) Several authors used acetic acid or a mixture of acetic acid and other solvents (*4*, *32–34*, *39*, *56*, *59*, *70*, *77*). The alcohols have found wide use for the determination of acids and bases (*10*, *15*, *38*, *68*, *69*, *80*). Chloroform has been used (*14*, *32*, *41*, *50*, *51*), but generally because of its specific solvent power for the system under study. Fritz has demonstrated that a variety of solvents may be used (*22*). Other solvent systems are reported (*17–20*).

INDICATORS AND ELECTRODES

Kolthoff (*42*) proposed a definition of an indicator for acid-base titration in any solvent system, as "weak acids or weak bases, the

acid form of which has a different color from the basic form." The principles and use of indicators in water (*47*) may be used as a guide to the development of a like system of indicators for nonaqueous solvents.

Kolthoff (*43*) stated that the present choice of indicators is more than adequate to satisfy all the needs of aqueous media, but not for nonaqueous media. Davis and Schumann (*13*) stated, "Although academic studies have thrown considerable light on the subject . . . there is a great need for further investigation of acid-base phenomena in various solvents . . . Before acid-base measurements in organic solutions can be performed as readily as those in aqueous solutions, it will be necessary to provide a series of indicators ranging from strongly acidic to strongly basic compounds."

There is no absolute criterion of acidity or basicity in nonaqueous solutions. Acids and bases of unlike nature may undergo a change in the relative position of their respective strengths in different solvents. All information reported to date has concerned the H-acids of Brønsted. No information is available for the non-H-acids of Lewis, such as boron trifluoride, aluminum chloride or antimony trichloride.

A satisfactory means has not been found to determine absolute acid or base strengths in a variety of solvents. New electrode systems that do not have liquid junctions, or whose liquid junction is small and can be estimated reliably, must be developed. Potential measurements have been made with the calomel-glass electrode system in acetic acid. These measurements cannot be interpolated into any absolute values for strengths of acids or bases.

Some studies of indicators have been made in specific solvents. Conant and Hall (*11*) studied ten indicators of two structural types in acetic acid. Kolthoff and Gauss (*45, 46*) determined the thermodynamic ionization constants of several indicators in both methyl and ethyl alcohols. It was found that the indicators had about the same ionization constants in both alcohols. Davis and Schumann (*13*) studied the behavior of bromophthalein magenta with different classes of organic bases in several aprotic solvents. In addition to the usual use of indicators in acid-base titrations, they may be used for quantitative comparison of base strength and for measurement of the relative strengths of organic acids.

Tomicek (*70*) observed that *p*-aminophenylbenzenesulfonamide, 1-naphthyl-6-sulfonamide, and 1-naphthyl-7-sulfonamide in acetic acid solution fluoresced in ultraviolet light. These compounds produced so strong a fluorescence and such a marked change at the equivalent point that they could be titrated visually with perchloric acid under ultraviolet light. The fluorescent color change was used as the indicator.

Methods for acid-base titrations have been reported which employ the following indicators: modified methyl orange (xylene cyanol) (*20*), methyl red (*20, 60*), thymol blue (*22, 50, 51, 58*), methyl violet (*21, 33, 39, 77*), 1-naphtholbenzein (*32, 33, 59, 70*), bromocresol yellow (*38*), crystal violet (*56, 59, 67, 70*), phenolphthalein (*58*), benzyl auramine (*59*), methyl orange (*60*), and cresol red (*70*).

Hall and Conant (*25*) based their work in acetic acid on measurements with the chloranil electrode.

Most of the early potentiometric measurements were made using a lithium chloride bridge. Clarke, Wooten, and Compton (*10*) appeared to be the first to use both electrodes in the titration vessel. Fritz and Lisicki (*22*) used a pH meter and glass-antimony electrodes. Markunas and Riddick (*56*) used a calomel-glass electrode system in acetic acid. Moss, Elliott, and Hall (*58*) used the antimony-antimony system in ethylenediamine, and found that the glass-antimony system was not suitable. Palit (*60*) used the calomel-glass electrodes in the G-H solvent. Ruehle (*66*) studied potentiometric titrations in a number of amphiprotic solvents with the saturated calomel-quinhydrone electrodes. Seaman and Allen (*67*) used a glass-calomel system with the calomel electrode immersed in saturated potassium chloride. The calomel electrode was connected to the titration vessel by a bridge of acetic acid saturated with lithium chloride. Tomicek (*70*) compared the quinhydrone, chloranil, and glass-calomel electrodes. Virasoro (*73*) studied titration with calomel-agar, silver, and silver-silver chloride in butyl alcohol.

TITRANTS

Perchloric acid is the strongest acid in organic solvents and has been found to be the most suitable acid titrant in acid type amphiprotic solvents. Perchlorates have a more favorable solubility than the salts of any other acids. Hydrochloric acid is unsuitable in many solvents because of its high fugacity and the insolubility of many chlorides. Sulfuric acid introduces complications, including unfavorable solubility of sulfates. Lavine and Toennies (*51*) found that perchloric acid slowly hydrolyzed acetonitrile and titrant solutions of perchloric acid in acetonitrile could not be used unless freshly prepared and standardized. Perchloric acid in acetic acid has been used for the determination of a wide variety of materials (*4, 20, 21, 32–34, 39, 56, 59, 70, 77*).

The most widely used bases for amphiprotic solvents, particularly the alcohols, are alkali metal alkoxides and alkali metal hydroxides. Potassium hydroxide appears to be more suitable than sodium hydroxide. The sodium or potassium alkoxides are more generally used (*22, 38, 50, 51*). Palit (*60*) used sodium hydroxide in the G-H solvent. Moss, Elliott, and Hall (*58*) found sodium aminoethoxide ($H_2NCH_2CH_2ONa$) to be a suitable titrant in ethylenediamine.

Wooten and Ruehle (*80*) found that solutions of both potassium hydroxide and sodium butoxide in butyl alcohol were oxidized by the oxygen in the air. It was concluded that butyric acid was formed because titrations of strong acids such as picric, dichloroacetic, and trichloroacetic in butyl alcohol gave two inflection points. Weak acids such as acetic and phenylacetic gave only one inflection point because butyric acid is of about the same strength. Commercial butyl alcohol showed the inflection points with picric acid with freshly made titrant. Freshly made titrant from purified butyl alcohol showed only one inflection point with picric acid. Further work showed that butanolic solutions of sodium butoxide are more stable than those of potassium hydroxide. The butoxide solution can be kept in a reducing atmosphere when protected from light.

There is no acid that is as satisfactory for use in aprotic solvents as perchloric acid is for amphiprotic solvents. The first known reported acid-base titration in nonaqueous solvents was with hydrogen chloride in benzene. This solution changed titer too rapidly to be practical. The sulfonic acids have found wide acceptance because they are nonvolatile and stable, and have a favorable solubility. *p*-Toluenesulfonic acid in chloroform was used by Dietzel and Paul (*14*). Its use was confirmed by Khait (*41*). Trautner and Neufeld (*71*) and Trautner and Shaw (*72*) further studied the use of this acid. Trautner and Shaw developed a method for producing a pure, dry acid. Purified *p*-toluenesulfonic acid monohydrate was heated at 120° C. at reduced pressure. Air dried over phosphorus pentoxide was bled into the drying chamber to maintain the pressure at 10 mm. The product is relatively nonhygroscopic and can be kept in a well-stoppered bottle. This acid appears to be the most satisfactory acid for most titrations in aprotic solvents, but at present it is necessary to purify and dehydrate the commercial product before use (*13*).

Trichloroacetic, *d*-camphorsulfonic, and picric acids have been used as titrants to demonstrate the applicability of bromophthalein magenta as an indicator in aprotic solvents (*13*).

Derivatives of guanidine appear to be the most satisfactory base titrants in aprotic solvents. Davis and Schumann (*13*) have shown that 1,3-diphenyl-, di-*o*-tolyl-, and dicyclohexylguanidine appear to be the strongest bases in benzene. The latter is too difficult to dissolve to be practical. It is fairly soluble in chloroform but reacts with the solvent, particularly when warmed.

STANDARDS

The standards suitable for aqueous solutions are generally suitable for nonaqueous solutions. Diphenylguanidine prepared according to Carlton (*9*) has been used by several investigators. Its favorable solubility makes it particularly adaptable for standardizing acids in aprotic solvents. Fritz (*20*) standardized perchloric acid in *p*-dioxane with diphenylguanidine. Two compounds that were known to be of high purity were titrated with the standard acid. The following is a summary of the results:

	Determinations	Mean, %	Range, %	Mean Deviation, %
2,2′-Bipyridine	4	99.44	0.19	0.08
Brucine	3	99.97	0.19	0.06

Benzoic acid of reagent grade or National Bureau of Standards standard sample has been used for standardizing bases (*22*, *38*, *68*).

Sodium carbonate was one of the first substances to be used for standardizing nonaqueous acid solutions and still finds wide acceptance (*4*, *36*, *67*, *70*, *77*).

Potassium acid phthalate is a reliable standard for perchloric acid in acetic acid. Seaman and Allen (*67*) studied this standard both potentiometrically and with crystal violet indicator. They standardized a solution of perchloric acid potentiometrically with both NBS potassium acid phthalate and sodium carbonate prepared according to Kolthoff and Sandell (*48*). A difference of 9 parts in 11,000 was found between the averages. The data are given in the next section. Markunas and Riddick (*56*) standardized perchloric acid with the same standard in a study of the scope of titrimetry in acetic acid. The two papers appeared almost simultaneously.

ACCURACY AND PRECISION

The accuracy and precision of acid-base titrations in nonaqueous solvents are of the same order as analogous titrations in water.

Seaman and Allen's potentiometric standardizations of perchloric acid with potassium acid phthalate and sodium carbonate illustrate both the precision and accuracy obtainable with careful technique (*67*). Their data follow:

	Na_2CO_3, *N*	$KHC_8H_4O_2$, *N*
	0.11747	0.11762
	0.11736	0.11753
	0.11748	0.11747
	0.11749	0.11747
	0.11730	0.11764
	0.11745	0.11740
Average	0.11743	0.11752
Range	0.00019	0.00024
Standard deviation	±0.00008	±0.00009

All compounds do not titrate sharply in a nonaqueous system. This is a familiar situation in the aqueous system. The accuracy of titrating such compounds may be increased by either potentiometric titrations or the use of a reference buffer solution containing the indicator. The buffer solution is prepared to have the same indicator color as that of the pure compound at its equivalent point when titrated. Methyl nicotinate when titrated with perchloric acid in acetic acid give a sluggish end point. Seaman and Allen (*67*) prepared two reference buffer solutions of different chemical composition for the titration of methyl nicotinate. The base was carefully purified by fractional distillation and the apparent purity, determined by titration in aqueous solutions, was found to be 100.2 and 100.3%; water by the Karl Fischer method, 0.02%. Titration to the standard buffer color No. 1: 100.3, 100.2, 100.1, 100.0, 100.2, 100.5%; average 100.2%; range 0.5%; standard deviation ±0.2. Values for standard buffer No. 2 were 99.9, 100.2, 100.3%; average 100.1%; range 0.4%; standard deviation ±0.2%.

For routine types of analysis for substances that act as strong bases in acetic acid Markunas and Riddick (*56*) report a reproducibility of about 0.2%. This conclusion was based on the results of titration of substances that act as strong bases in a survey analysis of about 400 compounds. Other investigators report the same order of accuracy and precision in acetic acid (*59*, *70*).

Semimicro- and microtitrations in acetic acid have about the same range of error as similar titrations in aqueous solutions (*39*).

Fritz (*20*) used perchloric acid in *p*-dioxane and ethyl ether and obtained results comparable to those made in a similar manner in aqueous solutions.

Clarke, Wooten, and Compton (*10*) studied the reproducibility of potentiometric titrations in butyl alcohol using potassium hydroxide in butyl alcohol as the titrant. Five aliquots of NBS benzoic acid solution were titrated. The volumes of titrant used were 17.34, 17.34, 17.39, 17.37, 17.35 ml.; average 17.36 ml.; range 0.05 ml.; standard deviation ±0.022 ml.

The error in titrations in the G-H solvent is of the same order as reported by others for routine type determinations (*60*).

Davis and Schumann (*13*) made a series of experimental semimicro titrations in benzene to demonstrate the applicability of the indicator bromophthalein magenta. The reproducibility reported was good.

METHODS

The coefficient of expansion of nonaqueous solvents is considerably greater than that of water. For precise results, the titrant must be kept and used at a constant temperature or a temperature correction must be applied. Seaman and Allen (*67*) assumed that perchloric acid solution in acetic acid had the same coefficient of expansion as acetic acid—namely, 0.0011 per 1° C.

Titrations in Acetic Acid. The potentiometric and indicator methods given by Markunas and Riddick (*56*) are essentially those used by Nadeau and Branchen (*59*), Blumrich and Bandel (*4*), Seaman and Allen (*67*), Kahane (*39*), and Fritz (*21*).

Potentiometric Method. A sample containing about 3.5 milliequivalents of the material to be analyzed is weighed into a 250-ml. tall-form beaker, without spout, and dissolved in 30 ml. of acetic acid, warming if necessary. The mixture is then cooled and titrated potentiometrically.

Indicator Method. The same weight of sample as required for the potentiometric method is weighed into a 250-ml. Erlenmeyer flask and dissolved in 30 ml. of acetic acid. One drop of crystal violet solution (1% in acetic acid) is added and the solution is titrated with 0.1 *N* perchloric acid in acetic acid to a blue green color. The range of color change for crystal violet is rather broad. In order to become familiar with the end-point color, several potentiometric titrations with indicator present should be made.

Salts of Carboxylic Acids. The major limitation for the determination of salts of carboxylic acids is their solubility in acetic acid. Most carboxylic acid salts of lithium, sodium, potassium, ammonium, primary, secondary, and tertiary amines, and quaternary salts of amines have sufficient solubility to be titrated (*4*, *56*, *70*). Some salts of calcium can be titrated (*56*).

Amines. Amines, their derivatives and similar compounds, and their carboxylic acid salts can be determined (*4*, *56*, *70*). Blumrich and Bandel (*4*) report an acetylation method for the determination of tertiary amines in a mixture of amines.

Amino Alcohols. This class of compounds can be titrated readily (*56*).

Oxazolines. The only known successful method for analyzing oxazolines is by titration in acetic acid (*56*).

Amino Acids. Nadeau and Branchen (*59*) demonstrated the practicability of determining amino acids by studying eleven representative ones.

Amides of Carboxylic Acids. These compounds as well as acetylated amines cannot be determined (*4*).

Chlorides, Bromides, Nitrates, and Sulfates. These salts of the alkali metals, ammonia, and amines have been titrated by

Higuchi and Concha (*33*, *34*), using a modification of the method given above (*56*). Sulfates presented considerable difficulty because of their insolubility in acetic acids. Some of the compounds analyzed were sodium, potassium, ammonium, procaine, and histidine chlorides, ammonium, sodium, and pilocarpine nitrates, codeine and histamine phosphate, and quinine sulfate.

QUININE. Quinine in mixtures can be extracted from an ammoniacal solution with chloroform, the chloroform evaporated, and the alkaloid dissolved in acetic acid and titrated. A method is given for the separation and determination of a mixture of quinine and strychnine (*32*).

ALKYLENE OXIDES. These oxides react with aniline hydrochloride in acetic acid, liberating aniline which can be titrated (*4*).

NICOTINIC ACID, NICOTINAMIDE, AND RELATED COMPOUNDS. Kahane (*39*) has developed micro- and semicro methods. He applied the titration in acetic acid as part of a method for analyzing crude products containing nicotinic acid, nicotinamide, and sodium, calcium, and ammonium nicotinates.

SULFONAMIDES. The behavior of eight sulfonamides when titrated in acetic acids was studied by Tomicek (*70*). The stronger bases may be titrated with crystal violet as indicator; the weaker ones are best titrated potentiometrically. Sulfonamides derived from naphthalene were titrated by using their distinct change in fluorescence at the equivalent point.

BASIC NITROGEN IN OILS. Wittmann (*78*) has described a rapid, exact potentiometric determination of basic nitrogen in hydrocarbons and hydrogenated coal oils. The oil does not have to be completely soluble in the acetic acid, as the basic nitrogen compounds are immediately extracted into the acid phase. An accuracy of ±0.2 mg. of ammonia per liter can be obtained. Wilson (*77*) described a method for trace organic bases in aromatic and aliphatic hydrocarbons using 0.02 *N* perchloric acid and methyl violet indicator. He found that the presence of a hydrocarbon increased the sharpness of the end point. The end point is sharp to ±0.02 ml.

G-H Solvent. The mixture Palit (*60*) found most suitable was a 1 to 1 mixture of ethylene glycol or propylene glycol and isopropyl alcohol. The proportion of isopropyl alcohol can be varied from 15 to 70% v. Perchloric acid was found most suitable as the titrant. Methyl red was the preferred indicator, although methyl orange could be used. A pH meter with glass and calomel electrodes was used for potentiometric titrations. The G-H mixture was regarded by Palit as an almost universal solvent for alkali metal salts of monobasic organic acids.

ALKALI METAL SALTS OF MONOCARBOXYLIC ACIDS. Sodium salts of acetic, propionic, butyric, benzoic, cinnamic, mandelic, oleic, and stearic acids titrated satisfactorily.

AMINES. Strychnine and brucine titrated with the sharpest end point, that for aniline was fairly sharp, and the error for quinoline, naphthylamine, *p*-toluidine, and pyridine was too large for this solvent to be of practical use.

MIXED ACIDS. Acid mixtures such as nitric and acetic, sulfuric and acetic, gave two and three inflection points, respectively, on the titration curve when titrated with sodium hydroxide.

SALTS OF INORGANIC ACIDS. Salts of the general formula *X*OONa, where *X* is any negative element, are highly soluble in the G-H solvent and can be titrated accurately. Such salts include metaborates, aluminates, nitrites, nitronates, hypophosphites, hyposulfites, sulfinates, and chlorites. In addition borates, silicates, arsenates, etc., can be titrated.

BORIC ACID. This is a strong acid in the G-H solvent.

ALKALI IN SOAP. Free alkali in soap can be readily measured.

EQUIVALENT WEIGHT. The equivalent weight of high molecular weight fatty acids may be determined by a modification of the basic procedure.

Methanol-Benzene (1 to 1). Fritz and Lisicki (*22*) reported titrating several classes of compounds in this solvent using a sodium methylate–solvent mixture as the titrant. A pH meter with antimony-glass electrodes was used. Lithium chloride was added to reduce the resistance of the solution.

CARBOXYLIC ACIDS. Salicylic, benzoic, *p*-aminobenzoic, and stearic acids can be successfully titrated.

ACID CHLORIDES AND ANHYDRIDES. These behave as strong monobasic acids. 3,5-Dinitrobenzoyl chloride, benzoyl chloride, and phthalic anhydride have been titrated.

ENOLS. Methone (dimethylcyclohexanedione) was reported.

Monobutylamine. This solvent was used by Fritz and Lisicki (*22*) to titrate weakly acidic compounds. The titrant was the same as the one used for the methanol-benzene system. Antimony-glass electrodes were used.

ENOLS. Acetylacetone was reported.

PHENOLS. Phenol was reported.

Pyridine as Solvent. The general use of pyridine is the same as for butylamine (*22*).

HYDROXYLAMMONIUM SALTS. The hydrochloride has been successfully titrated in this solvent.

Alcohols. COMMERCIAL DIMETHYL SULFATE. A procedure for the determination of methyl hydrogen sulfate and sulfuric acid in commercial dimethyl sulfate dissolved in methanol has been reported (*38*).

Acidity of Oils. This subject was one of the first applications of titrations in nonaqueous solvents (*1*) and has received considerable attention (*10*, *68*).

Chloroform. Folin and coworkers (*17–19*) studied acid-base titrations in nonaqueous systems.

ACIDS. All classes of acids can be titrated with sodium ethylate in organic solvents. Those acids not readily soluble in chloroform can be dissolved in 10 ml. of absolute alcohol and diluted to 100 ml. with chloroform.

ALKALOIDS. *p*-Toluenesulfonic acid in chloroform was used as the titrant and methyl yellow as the indicator. Specific directions have been given for the determination of alkaloids in drugs and alkaloidal preparations (*14*). Khait (*41*) has refined and extended the work of Dietzel and Paul (*14*) for the extraction and determination of alkaloids.

AMINES. Dietzel and Paul (*14*) have determined aliphatic and aromatic primary, secondary, and tertiary amines by the titrimetric procedure used for alkaloids. Hexamethylenetetramine titrates as a monoacid base.

EFFECT OF WATER. This subject has received little quantitative attention. Markunas and Riddick (*56*) found that large amounts of water in acetic acid gave high results, but amounts up to approximately 1.5% of the original solvent (about 30 ml.) did not affect the accuracy of the determination. Fritz (*21*) found that about 3% can be tolerated.

From the description of the solvents reported by the different workers it can be concluded that water is more harmful in aprotic than in amphiprotic systems. It appears that some titrants can be used in benzene or chloroform saturated with water. The limits of water reported by Riddick and Markunas and by Fritz appear to be the limits for other amphiprotic solvents. Unless definite proof has been obtained, it is advisable to keep the water content low.

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AMPEROMETRIC TITRATIONS

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FROM the number of papers that have appeared since the first review in 1949 (*42*), it is evident that the amperometric titration method is gaining momentum and is rapidly attaining maturity as a widely accepted analytical method. Several general and review papers have been published (*3, 10, 23, 31, 32, 35, 40, 59, 65, 80*).

APPARATUS AND METHODOLOGY

Delahay (*14*), Ringbom (*67*), and Gentry and Newson (*21*) described circuits suitable for amperometry. Heyrovský (*28*) has suggested an oscillographic technique for end-point detection. Rius and Serrano (*69*) used a milliammeter with the dropping mercury electrode in the titration of solutions of relatively high concentration. Parks and Lykken (*60*) have described the adaptation of amperometric titrations to operations on a reduced scale.

Laitinen and Burdett (*43*) designed a cell with a shielded dropping electrode for the continuous passage of nitrogen during a titration. Berman, Saunders, and Winzler (*2*) suggested a vibrating mercury electrode for polarographic measurements with moving solutions, but did not apply it to amperometric titrations. Elofson and Mecherly (*17*) designed a special cell for use at low temperatures.

Vibrating platinum electrodes have been used by Harris and Lindsey (*27*) and by Rosenberg, Perrone, and Kirk (*70*). Vyakhirev (*79*) used lead electrodes for the titration of sulfate with lead.

Tomicek, Blazek, and Roubal (*77*) performed amperometric titrations with bromine in glacial acetic acid. Lyalikov (*50*) titrated silver nitrate with potassium hydroxide in fused nitrate, using a platinum indicator electrode. Fused potassium nitrate–potassium hydroxide mixtures proved superior to fused potassium hydroxide as a reagent because of their less hygroscopic character.

A technique somewhat related to the amperometric and dead-stop methods has been recently devised by Reilley, Cooke, and Furman (*64*), and named the derivative polarographic titration. The electromotive force necessary for the passage of a constant, predetermined current is measured. This quantity is related to the slope of the current-voltage curve at the zero current point.

Ringbom (*68*) has devised a technique involving the use of "amperometric indicators." A small amount of polarographi-

cally active substance is added to serve as an indicator for titrations involving substances not yielding suitable polarographic waves.

ION COMBINATION REACTIONS

The determination of sulfate in a zinc plating bath by titration with 1 *N* lead in the presence of ethyl alcohol to decrease the solubility of lead sulfate has been described by Korshunov and Sazanova (*41*). Vasil'ev and Getsova (*78*) found acetone preferable over ethyl alcohol in the determination of sulfate in fluoride and aluminate solutions.

Lead electrodes have been used by Vyakhirev (*79*) for the titration of solutions 0.1 *N* or more in sulfate ion with lead ion. It was necessary to wait 20 to 30 seconds after each addition for a steady current.

Lead ion has been used as a reagent for tungstate ion in 50% ethyl alcohol medium by Kalvoda and Zyka (*30*). The same authors investigated the titration of thallium with iodide and with dichromate in acetone-water medium, and silver ion with thiocyanate, ferrocyanide, and nitroprusside.

The titration of lead ion with dichromate, using a milliammeter switched in only at the movement of measurement, was described by Rius and Serrano (*69*). The results were correct within ±5%.

The titration of phosphate with uranyl ion has been applied by Boos and Conn (*4*) to the determination of total phosphorus in organic compounds.

Ferrocyanide has been used by several investigators as a precipitating reagent for copper. Chovnyk and Klebs (*11*) recommended the use of a hydrochloric acid solution in the presence of 1.0 to 1.5 *M* potassium salt to approach the composition $5Cu_2Fe(CN)_6 \cdot K_4Fe(CN)_6$. In the absence of alkali metal the precipitate was $Cu_2Fe(CN)_6$, but the curves were irregular and poorly reducible. Riccoboni and Goldschmied (*66*) reported $Cu_2Fe(CN)_6$ as the product, but in the reverse titration obtained $K_2Cu_3[Fe(CN)_6]_2$ in neutral solution and the normal salt in the presence of acid or ammonium chloride. Kalvoda and Zyka (*30*) titrated copper in 1 *N* acetic acid or 0.5 *N* acetic–0.5 *N* nitric acid. They found irregular behavior in the presence of potassium salts.

Nimer, Hamm, and Lee (*57*) titrated zinc in 1.7 *M* ammonium acetate, and indium in 0.1 *M* potassium chloride with potassium ferrocyanide, obtaining in both cases the normal salt, rather than the double potassium salts. Riccoboni and Goldschmied (*66*) found zinc to give the normal salt in neutral or ammoniacal medium, but obtained $K_2Zn_3[Fe(CN)_6]_2$ in acid solution. Butenko and Rynskaya (*8*) used a rotating platinum electrode to titrate zinc with ferrocyanide. Best results were obtained in acid solution. Sodium or potassium salts led to high results.

Potassium ferricyanide was used as a precipitant by Chovnyk and Kuz'mina (*12*) who observed $Ni_3[Fe(CN)_6]_2$ as the product in the titration of 0.01 *M* nickel sulfate under various conditions of electrolyte. The sensitivity could be increased by use of the rotating platinum electrode. Zinc in hydrochloric acid or potassium chloride solution, and copper alone and in the presence of ferric iron (using fluoride as a complexing agent) likewise gave the normal ferricyanides.

Liberti and De Cesaris (*48*) described the titration of copper with thiocyanate in slightly acid or neutral solution, after reduction to copper(I) with hydroxylamine.

Fluoride was titrated with thorium ion by Luzina (*49*). Amounts of 0.005 to 1 mg. of fluoride could be successfully determined. Aluminum, magnesium, arsenate, and phosphate interfered. Fluoride was titrated with 0.2 *N* lead nitrate in the presence of chloride to precipitate lead chlorofluoride by Petrow and Nash (*61*). Under suitable conditions, as little as 0.5 mg. of fluoride could be determined to an accuracy of 0.5% or better.

Fluoride has been used as a reagent by Ringbom and Wilkman, who used ferric chloride as an "amperometric indicator" (*68*). Aluminum was titrated to AlF_3^{---} at pH 2.5 to 3.5. To determine magnesium, the sample was added to a measured excess of fluoride, giving MgF_3^-, after which an excess of aluminum was added, and titrated as above. Calcium was determined by precipitation as the fluoride. Ringbom and Wilkman (*68*) also determined calcium by titration with oxalate, using cadmium ion as the indicator ion.

The use of hexamminecobalt(III) ion as a precipitant for ferrocyanide and pyrophosphate has been described by Laitinen and Burdett (*44*). The normal ferrocyanide was observed, but the ratio of cobalt to pyrophosphate was 4 to 3 only in the absence of sodium salts. In the presence of sodium ion, which is the recommended condition, the ratio was 1 to 1, corresponding to the precipitate $Co(NH_3)_6NaP_2O_7$. The salt $Co(NH_3)_6BrSO_4$ proved to be too soluble to permit the titration of sulfate ion in the presence of an excess of bromide ion.

OXIDATION-REDUCTION REACTIONS

The reaction between ferrous iron and dichromate has been the subject of several recent papers. Kolthoff and Medalia (*37*) studied the titration of ferrous iron in 70 to 80% acetone using the rotating platinum electrode at a potential of +0.7 volt *vs.* the saturated calomel electrode. While no constant diffusion current region was observed, the titration curves were satisfactory. Butenko and Bekleshova (*6*) determined manganese, chromium, and vanadium in steel by titration with ferrous sulfate after oxidation with persulfate to determine the sum of manganese, chromium, and vanadium; after reoxidation with persulfate and destruction of the permanganate with chloride to determine chromium and vanadium; and after permanganate oxidation and reduction of the excess with oxalate or nitrite to determine vanadium. Grenberg and Genis (*25*) found this procedure to give satisfactory results, using the rotating platinum electrode at a potential of 1.0 volt. Parks and Agazzi (*58*), in a similar procedure, determined chromium and vanadium in steel and petroleum by oxidizing the chromium and vanadium with perchloric acid followed by permanganate. After determining the total chromium and vanadium, they reoxidized the vanadium with permanganate, destroyed the excess with sodium azide, and titrated again, using a rotating platinum electrode.

The use of vanadium(II) solution for the amperometric titration of ferric iron and of chromate ion in thiocyanate medium was mentioned by Meites (*55*).

Marks and Glass (*51*) determined residual chlorine in water by titration with arsenite using a gold electrode. Total chlorine was determined by titration in the presence of iodide. In the absence of iodide, only free chlorine was determined. Marks and Joiner (*52*) determined residual chlorine in sewage by treating the sample with a measured excess of phenylarsene oxide, followed immediately by potassium iodide. The unreacted phenylarsene oxide was titrated with iodine.

Haller and Listek (*26*) determined various active chlorine compounds in water by amperometric titrations. After the addition of sodium hydroxide, and adjustment of the pH to 7, an arsenite titration yielded the sum of chlorine and hypochlorite. A second portion made alkaline, adjusted to pH 7, and treated with iodide, was titrated with arsenite to determine chloramine as well as free available chlorine. A third portion was adjusted to pH 7 without the alkali treatment, treated with iodide, and titrated. Chlorine dioxide reacts with iodide to yield chlorite. Consequently, one fifth of the oxidizing power of chlorite was determined in addition to the above. Finally, the total oxidizing power was determined by adding iodide at a pH of 2 and titrating with arsenite.

Evans and Simmons (*18*) improved the sensitivity of the Winkler method for oxygen determination by adding an excess of thiosulfate and titrating with standard iodine. The amperometric end point for the iodine-thiosulfate reaction has been used by Laitinen and Burdett (*45*).

Rius and Serrano (*69*) titrated arsenite with bromate using a milliammeter connected momentarily during the measurement.

Goffart, Michel, and Pitance (*24*) titrated manganese(II) to the pyrophosphate complex of manganese(III) using platinum and silver wire indicator electrodes. Goffart (*22*) described a similar titration of cerium(III).

TITRATIONS INVOLVING ORGANIC REAGENTS

Stock (*75*) determined milligram and microgram quantities of copper, zinc, or cadmium by titration with 8-quinolinol (oxine). Copper could be determined in the presence of cadmium, but not in the presence of zinc. Cadmium could be determined in the presence of either copper or zinc. Zan'ko and Panteleeva (*82*) titrated the sum of copper and zinc in an acetate buffer of pH 5, and copper in the presence of zinc in a biphthalate buffer of pH 2.8. Iron when present precipitated in both buffers. Ishibashi and Fujinaga (*29*) titrated magnesium with oxine in an ammonium hydroxide-ammonium chloride buffer at a concentration of 0.001 *M* with an accuracy of 0.7% or better. Calcium was removed by adding an excess of ammonium oxalate.

Quinaldic acid was used by Stock (*73*) in the determination of copper and zinc. Precipitation was slow at room temperature but practicable at 60° C. Alternatively, an excess of reagent could be added and a back-titration performed at room temperature with copper or zinc solution. Under certain conditions, copper and zinc could be successively titrated. Copper could be determined in the presence of cadmium, but the determination of cadmium was not successful. Stock (*74*) titrated copper with quinoline-8-carboxylic acid without interference from zinc, cadmium, ferrous iron, cobalt, nickel, or lead.

Liberti and Cervone (*47*) titrated copper with 2-mercaptothiazole in amounts of 0.7 to 5 mg. with an accuracy of 1%. Cadmium and manganese interfered. The reagent was assayed by titrating with silver ion, using the rotating platinum electrode. Calzolari (*9*) titrated copper with dimethyldithiohydantoin. In hot solution, a compound of 1 mole of copper to 1 mole of reagent residue was obtained.

Kolthoff and Liberti (*36*) determined copper(II) and iron(III) by titration with cupferron. Copper(II) was titrated in various buffers of pH 5 to 6, while iron(III) was determined in citrate or tartrate buffers of pH 3 to 4. Copper was determined in the presence of large amounts of iron(III) by using a citrate buffer which was made 0.5 *M* in potassium hydrogen fluoride. Iron could be determined in the presence of an equal or lesser quantity of copper by titration in 0.1 *N* hydrochloric acid medium. The end point was found before the precipitation of copper began.

Sandberg (*71*) described the titration of cadmium with naphthoquinoline in the presence of iodide. Zinc does not interfere, but ferric iron must be reduced with hydroxylamine. Various heavy metals could be removed by reduction with iron wire. He also titrated iron(III) with 5,7-dibromo-8-quinolinol, taking precautions to prevent reduction of the iron by mercury. Copper and vanadium interfered. The titration of potassium ion with dipicrylamine in the presence of up to 15 times its concentration of sodium was also described.

Butenko *et al.* (*7*) determined nickel in steel by titration with dimethylglyoxime using alcoholic or alkaline solutions.

Pribil and Matyska (*62*) titrated bismuth, iron(III), nickel(II), lead, zinc, and cadmium with the disodium salt of ethylenediaminetetraacetic acid (Versene) at various pH values and applied potential depending upon the metal ion being titrated. Bismuth could be determined in the presence of most ions at a pH of 1 to 2. A procedure was worked out for the determination of bismuth in lead.

DETERMINATION OF SULFHYDRYL COMPOUNDS

Benesch and Benesch (*1*) applied the silver titration method of Kolthoff and Harris (*34*), using the rotating platinum electrode, to the titration of sulfhydryl groups in amino acids and proteins. Using a microburet with 0.001 *N* silver nitrate, amounts down to 0.03 mg. of mercaptan sulfur could be successfully determined in thioglycolic acid, cysteine, glutathione, and ergothioneine. Egg albumin, bovine serum albumin, human serum albumin, and various dialyzed sera were analyzed for sulfhydryl content. Frank *et al.* (*20*) reported low results in the titration of certain mercaptans by the silver titration method. Strafford, Cropper, and Hamer (*76*) showed that the low results were due to oxidation. Rosenberg, Perrone, and Kirk (*70*) modified the Kolthoff and Harris method by using a vibrating platinum electrode and adding the solution from a horizontal microburet. Microgram quantities of cysteine and glutathione could be determined.

Kolthoff and Harris (*33*) described a method for the determination of primary and tertiary mercaptans. All mercaptans react with silver in a molar ratio of 1 to 1. Primary mercaptans are oxidized by iodine to the disulfide, using 0.5 mole of iodine per mole of mercaptan, while tertiary mercaptans react with 1 mole of iodine to form the sulfenyl iodide. Mixtures of primary and tertiary mercaptans reacted with less than the calculated amount of iodine because of the partial formation of a mixed disulfide. In the presence of an excess of lead, the correct results were obtained because the mixed disulfide formation could be prevented by forming slightly dissociated mercaptides. The method is of limited accuracy because it is indirect and because some tertiary mercaptans react incompletely with iodine.

Kolthoff and Stricks (*38*, *39*) studied the reactions between copper(II) and cysteine in the presence of sulfite, and devised an amperometric titration for traces of cysteine and cystine using the rotating platinum electrode. The diffusion current corresponded to the reduction of copper(II) to copper(I) rather than to the metal. The over-all reaction is given by the equation

$$2Cu(II) + RS^- + SO_3^{--} = 2Cu(I) + RSSO_3^-$$

Cystine was determined by reduction to cysteine using sodium amalgam. Mixtures of cysteine and cystine were analyzed by titrations run before and after sodium amalgam reduction.

OTHER ORGANIC DETERMINATIONS

Duyckaerts (*15*) determined 8-quinolinol (oxine) and phenol, by titration with potassium bromate using a platinum indicator electrode in a rotating vessel. An accuracy of 0.4 to 0.5% was achieved.

Liberti (*46*) used a rotating platinum electrode to follow the titration of *p*-aminosalicylic acid with bromate in an acid solution containing bromide to produce 3-amino-2,4,6-tribromophenol. *m*-Aminophenol could be determined by the same method.

Elofson *et al.* (*16*, *17*) used an amperometric method to follow the titration of a coupler such as a pyrazolone or a naphthol with diazotized aromatic amines in well buffered solutions. A jacketed cell and buret were used to permit titrations at 0° to 5° C. A dropping mercury electrode at an applied potential of −0.2 to −0.3 volt was used.

COULOMETRIC DETERMINATIONS

Swift and coworkers have used an amperometric indication of the end point in several coulometric determinations with electrolytically generated reagents. Very sensitive determinations were worked out in favorable cases.

Using electrolytically generated bromine, Sease, Niemann, and Swift (*72*) determined thiodiglycol, Myers and Swift (*56*) determined arsenite, and Brown and Swift (*5*) determined antimony(III) by its oxidation to antimony(V) in hydrochloric acid medium. Wooster, Farrington, and Swift (*81*) oxidized iodide to iodine bromide using a similar technique.

Arsenite has been determined using electrolytically generated iodine (*63*) and chlorine (*19*).

Meier, Myers, and Swift (*53*) have described the coulometric determination of chromate and vanadate by use of electrolytically generated copper(I), with an amperometric end point.

Silver(II) proved to be an unsatisfactory intermediate for the

coulometric determination of manganese(II), arsenic(III), or cerium(III) because the rates of oxidation were too slow (*54*).

Cooke and Furman (*13*) used electrolytically generated iron(II) for the coulometric determination of cerium(IV) and chromium(VI), but used a potentiometric rather than an amperometric indication of the end point.

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CHROMATOGRAPHY

And Analogous Differential Migration Methods

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FOR the past 3 years, ANALYTICAL CHEMISTRY has presented extensive reviews devoted to the subject of chromatography and to special aspects of this field, such as paper chromatography and ion exchange methods (*63*, *195*, *315*, *335*, *350*). These and many other similar reviews have included a definition of terms, and a restatement of the principles of chromatographic separations as well as numerous examples of the resolution of mixtures (*57*, *116*, *196*, *198*, *333*, *335*, *366*).

In the past year, the utilization of chromatographic methods has continued at an accelerated pace in many fields ranging from physics to biology. These methods have been remarkably fruitful when applied to the investigation of the composition of plants and animals and when utilized for determination of the course of enzymatic reactions. Many of these applications involved minor modifications of the chromatographic technique, and they contributed little to our understanding of the principles upon which chromatography is based. As a consequence it is neither practical nor stimulating to continue tabulation of all the routine applications. Instead, it has seemed more profitable to compare a number of analogous analytical methods that depend upon the differential migration of the components of mixtures and to report the progress that has been made with the more promising of these techniques.

Most of these differential migration methods depend upon the physical properties of the substances to be separated from one another. Unlike chemical methods of analysis, these physical methods do not alter the substances being separated. By contrast with chemical methods that are restricted to use with particular substances, the differential migration methods are applicable to the extensive resolution of complex mixtures even when the nature of the constituents is unknown.

In the past decade the principles and the mechanism of chromatographic separations have been carefully examined (*57*, *87*, *88*, *117*, *125*, *163*, *198*, *241*). As a result, various differential migration methods may now be compared in relation to the principles and conditions employed for chromatographic separations. As a by-product, this approach may stimulate research on new methods for differential migration analogous to the methods already developed.

BASIS OF CHROMATOGRAPHIC SEPARATIONS

All chromatographic separations depend upon the differential migration of solutes through a polyphase system. The migration is effected by flow of solvent. This differential migration is determined by selective reversible distribution of the solutes between the fixed nonmobile phase and the mobile solvent, a liquid (*57*, *335*) or a gas (*160*).

From this view chromatography is a fractionation procedure. In this respect it resembles fractional distillation through a packed fractionating column wherein the migrating vapors are fractionated by selective distribution between the mobile gas phase and the refluxed liquid phase (*301*, *302*, *371*).

In a chromatographic column with a given chromatographic system (*57*, *335*), the rate of the migration of the solutes relative to the flow of the solvent is a property of the system itself, but the degree of resolution of a mixture depends upon the procedure employed for the migration. When a solution of a mixture is filtered through a column of sorptive material, some of the solutes are retarded in their migration, so that the leading boundary of each solute falls behind the leading boundary of the solvent itself. Determination of the migration rates by analysis of the effluent is called threshold analysis, break-through analysis, retardation analysis, and frontal analysis (*57*, *198*, *333*, *335*). This method of analysis provides much information about the rates of migration of the solutes, but it does not resolve the mixture.

For the extensive resolution of a mixture by chromatography, a small amount of the solution is added to the sorption column, so that it forms a narrow zone. The column is then washed with fresh solvent that forces the solutes in this zone to migrate through the sorptive phase. Because of their selective distribution between the two phases, the solutes migrate at different rates and separate from one another as a series of zones, each of which contains a single component of the mixture. The solutes in this sorptogram may be washed into the percolate one after another and collected separately as in elution analysis, or the sorptive phase may be removed and the solutes eluted from the separate zones with suitable solvents. This differential migration of an initially narrow zone permits the complete resolution of complex, multicomponent mixtures.

The formation of the sorptogram or chromatogram may be varied in many ways. Columns of different sorptive media and columns with sorption gradients may be employed (*335*). Mixtures of solvents with various affinities for the sorbent and for the solutes may be utilized in admixture or in succession. The effect of these variations is often an improvement in the sharpness of the zones and a more complete separation of the mixture.

SOLUTION BOUNDARIES IN POROUS MEDIA

In chromatography, the nonmobile phase plays an important though unspectacular role in addition to the selective sorption of the solutes. This phase prevents the mixing of the solutions of the several components that separate as zones in the column. In this way it permits the formation and maintenance of sharp boundaries between these solutions and the intervening zones of the solvent (*378*).

BASIS FOR COMPARISON OF DIFFERENTIAL MIGRATION METHODS

One condition common to chromatography and to analogous migration methods is the use of a driving force to effect the migration of the solutes. As a result, all these methods may be compared with respect to this force and its applicability. The migration methods may also be compared with respect to use with narrow and wide zones of the mixture, use with and without porous media, and in relation to the nature of the migration media.

The degree of resolution of mixtures by differential migration varies both with the forces that are employed and with the migration media. The sequences of the zones also depend upon both of these factors.

The medium in a differential migration system resists the migration of the mixture. The resistive force may vary with the solutes and with the medium. In chromatography, for instance, the resistive action of the sorbent retards the movement of some solutes more than others; hence it determines the segregation of the initial zone into the series forming the chromatogram. Here, as in many other examples of differential migration, the kinetic mechanism of the retardation is a complex dynamic distribution

[1] On leave from University of Wisconsin under Participating Institutions Program.

of the solutes between the two phases. Detailed theoretical treatments of these fractionating processes as countercurrent distribution are readily available (*57, 67, 69, 371*). For purposes of correlation, special emphasis is now placed upon the driving force rather than upon the more complex resistive forces.

The concept of a driving force and of a resistive force may be applied to the mechanism of a liquid-vapor fractionating column. The constituents of the mixture may be regarded as migrating through the column, with the less volatile constituents retarded to a greater degree than the more volatile constituents. In this case, the counterflow induced by gravity maintains the less volatile constituents stationary until all the more volatile ones have migrated through the column. The driving force is a temperature gradient.

When a single driving force is utilized to effect the migration of a mixture, the process is usually operated batchwise, producing complete resolution of the components contained in an initially narrow zone. Separations produced by application of a single driving force may also be carried out with continuous addition of the mixture, but under these conditions the components are often segregated into but two principal fractions. In a few cases, two driving forces may be applied simultaneously and at right angles, so that the migration process is carried out continuously with complete resolution of the mixture, which is added continuously as a narrow zone.

PRINCIPAL FORCES EMPLOYED FOR DIFFERENTIAL MIGRATION

Chemical potential gradients produce differential migration by diffusion. This force is operative to some extent in virtually all fractionation processes; in particular, it is responsible for the differential migration of solutes between phases not in equilibrium.

Simple diffusion results in the partial resolution of mixtures and in the establishment of frontal boundaries like those observed in a sorption column. This migration process is carried out conveniently in a porous or gelatinous medium, so that mixing is prevented (*259, 357, 378*). Because the initial zone of the mixture does not migrate, diffusion alone does not serve for the extensive resolution of multicomponent mixtures.

Diffusion with multistage apparatus, which involves forces in addition to chemical potential gradients, is an effective method for the resolution of mixtures of gases including isotopes.

Flow of solvent produces the migration of solutes in chromatography and in fractional extraction. The former is treated extensively in the following sections, and the latter is considered in the section devoted to counterflow processes. This kind of force may prove to be significant in conjunction with thermogravitational and electrogravitational separatory processes.

Gravity as a force for differential migration is restricted almost entirely to use with large particles. It has found most extensive use in metallurgy, particularly hydrometallurgy. It is the separatory force in flotation, sedimentation, settling, and sieving. It produces the countercurrent flow of at least one phase in several fractionating processes.

Centrifugal force serves for the separation of mixtures of large molecules and colloidal particles such as parts of plant and animal cells (*89, 178, 263, 283*). Usually a wide zone of the mixture is centrifuged, so that partial resolution is indicated by the migrating boundaries (*118, 231, 343*). In a few cases a narrow zone of the mixture has been layered above a layer of the solvent (*375*). This differential centrifugation might be improved a great deal by the use of porous media. Presumably the slower rate of sedimentation would be offset by better definition of the boundaries, especially when a medium with a density gradient is employed (*38*).

Electrical fields have found wide application to the separation of mixtures. They have been utilized for the resolution of mixtures of ions in gases and for the resolution of mixtures by migration from a narrow zone, an application that promises to be especially valuable in analytical chemistry when electrical migration in solution is combined with the use of porous or gelatinous media (see sections on electrical migration).

Temperature gradients are employed for the resolution of mixtures by distillation and by sublimation. In fractionating columns, gravity also plays a role, as indicated in the consideration of fractional distillation.

When phase equilibria are not involved, this kind of force leads to differential migration by thermal diffusion (Soret effect).

Magnetic fields have been utilized for the separation of large magnetic particles from nonmagnetic particles and for the deflection of charged, accelerated atomic particles. Magnetic fields have also been proposed as forces for the separation of ions in solution (*224, 335*). The paramagnetic properties of stationary ions in a nonuniform magnetic field or the magnetic properties of moving ions in a uniform field might be employed for this purpose. In either case, very powerful magnetic fields would be required (*90*).

MIGRATION METHODS UTILIZING VARIOUS DRIVING FORCES

Differential migration methods, the principal migration forces, and their applicability are summarized in Table I. More detailed comparison shows that chromatography is the most applicable of all the differential migration techniques. The applicability depends upon the nature of the mixtures to be resolved, the degree of resolution desired, and the facility with which the separation can be carried out.

It is not the purpose of this paper to treat all these differential migration methods, but rather to attempt an integration of the common principles, often obscured by the great diversity of apparatus and operations, developed for the various methods. As comprehensive reviews of familiar methods have been presented in this review series and elsewhere, the principal part of the review is devoted to chromatography and to its first cousin, electromigration in a porous medium. Some of the other methods, old and new, and their relation to chromatography, are considered later.

PROGRESS IN CHROMATOGRAPHY

In the past year many modifications and adaptations of chromatographic methods have been reported (*82, 131, 151, 162, 185, 244, 319, 385*). These include the use of chromatography for the examination of mixtures of a great variety of solutes. These applications have been based upon three principal modifications of the method—namely, paper chromatography, adsorp-

Table I. Applicability of Differential Migration Methods

Method	Principal Driving Force	Applicable to
Chromatography	Flow of solvent	All soluble substances, gases
Countercurrent extraction	Flow of solvent	All soluble substances, gases
Electromigration	Electrical field	Charged particles in solution or in suspension in liquids or gases
Electrochromatography	Electrical field	Charged particles in solution
Electrogravitational	Electrical field	Charged particles in solution
Fractional distillation	Temperature gradient	Liquids
Fractional sublimation (*106, 107, 287*)	Temperature gradient	Solids
Thermogravitational (Clusius column)	Temperature gradient	Gases
Diffusion (*72, 119, 136, 164*)	Chemical potential gradient	Solutions
	Pressure gradient	Gases
Mass diffusion (*22, 62*)	Chemical potential gradient	Gases
Sedimentation	Gravity	Particles in suspension
	Centrifugal	Particles in suspension and solution
Mass spectrometry (*4*)	Electrical plus magnetic fields	All substances capable of ionization in vacuum
Continuous electrochromatography	Flow of solvent plus electrical field	Charged particles in solution

tion and partition chromatography, and ion exchange chromatography.

Much advantage has been taken of paper chromatography for the separation of mixtures obtained from biological materials. These separations, which were reviewed by several workers (*63, 130, 333, 335*), are of great value in clinical investigations and in diagnosis. These uses of paper are especially versatile, as highly sensitive techniques have been developed for the detection of the zones of particular substances separated in the paper. In this connection considerable interest is attached to photometry (*251*), β-ray spectrometry (*252*), high frequency measurements (*307*), and the use of radioactive tracers, especially those produced in the mixture itself or in the developed paper chromatogram through irradiation with neutrons in the atomic pile (*108, 146, 352, 366, 378*).

Much of the older work on adsorption as applied to chromatography has been reviewed by Cassidy (*57*). The basic work on ion exchange and some of its applications to chromatography have been summarized by Kunin and Myers (*198*) and by others (*116, 195-197, 315, 350*).

EVOLUTION OF CHROMATOGRAPHY

Many recent reports (*96, 367, 368, 384*) indicate that the differential migration of solutes through porous media was known long before Tswett described his extensive chromatographic separation of leaf pigments in 1906. These early observations on the absorption of ions by soils (*198*), on the decolorization of solutions, and on the filtration of petroleum revealed that the filtration of a solution through an absorptive medium retarded the migration of the solutes, but this filtration method did not provide a resolution of complex mixtures of solutes.

Tswett showed that his columnar method for the separation of leaf pigments from one another depended upon the formation of a narrow initial zone of the mixture, followed by washing or development with fresh solvent. It was several decades before Tswett's novel analytical procedure was demonstrated convincingly to chemists, and it was not until 1941 that Schönbein's older partial separation of solutes by capillary ascent in paper was reported to be identical in principle with sorptographic separations effected in columns. It required a few more years before Liesegang utilized an initially narrow zone for the resolution of mixtures in paper and thereby laid the basis for paper chromatography. It was also Liesegang who utilized development from a narrow zone in a paper sheet with one solvent followed by transverse development with a second solvent and who thus extended, thereby, the sensitivity and the applicability of paper chromatography.

From the view set forth here chromatography is primarily an analytical procedure. The over-all mechanism is a repeated distribution or kinetic process dependent upon the reversible or dynamic fractionation of the solutes between the mobile and the fixed phases (*57, 335*).

VARIABILITY OF CHROMATOGRAPHIC SYSTEMS

For chromatographic separations, each phase may be a single substance or mixtures of two or more substances. The equilibria among solutes, solvent, and sorbent may involve solution, surface or interfacial attraction, and chemical reaction including solvation and complex formation in both phases.

Recently the basic information pertaining to the distribution equilibria in various chromatographic systems has been presented by Cassidy (*57*). He has attempted to describe the selective distribution of solutes between two phases in terms of the physical and chemical properties of the systems themselves. His book contains numerous references to the older literature pertaining to absorption phenomena and to the current uses of chromatographic methods.

From the practical point of view, the degree of variation of chromatographic systems is virtually unlimited. It is this very variability that makes chromatography so widely applicable and that defies most attempts at detailed interpretation in terms of the properties of the components of the chromatographic systems.

EQUILIBRIUM PHENOMENA AND MIGRATION RATES

For effective separations by differential migration in chromatographic systems, the solutes must be distributed dynamically between the two nonmiscible phases. For substances that are readily separable, it is not necessary for the solutes to be in true equilibrium. For substances that are difficultly separable, the widening of the zones that occurs when the solutes do not come to equilibrium results in inefficient separations.

Distribution equilibria of the solutes between the fixed and the mobile phase are a property of the system itself. The rate at which equilibria are established depends largely upon the nature, the dimensions, and the permeability of the particles themselves. This rate of distribution determines the rate at which the chromatogram may be formed. With leaf pigments adsorbed upon the impervious; granular surface-active particles of powdered sugar, an extensive separation of some twelve or more pigments may be effected in about 20 minutes. But with a column of similar length filled with permeable absorptive particles of commercial ion exchanger, a day or more may be required for the formation of the chromatogram.

DETECTION AND ISOLATION OF MINOR COMPONENTS BY CHROMATOGRAPHY

In most chromatographic separations, trailing portions of each zone of solute contaminate the following zones. These trailing portions may represent a small fraction of the major constituents of the mixture, but they sometimes represent a large fraction of the minor constituents. The properties of the chromatographic system limit the total amount of the mixture that may be added to a column or to a strip of paper; consequently they also limit the amount of the minor constituents that may be added. As a result, sensitive methods of detection must be employed for the location of these minor components of the mixtures. Owing to the trailing tendencies of the zones, the complete recovery of these minor constituents may be difficult or impossible, depending upon the nature and concentration of the solutes in the following zones. These trailing effects are usually negligible when the concentration of the solutes is sufficient to permit detection by chemical methods. They may be extremely troublesome when the minor constituents are barely detectable quantities of the radioactive elements (*338*).

In practice a minor constituent is usually most readily detectable when it forms the most absorbed or the least absorbed zone. As a rule a minor constituent is more completely recoverable when it forms the least absorbed zone.

ABSOLUTE SEPARATION OF MIXTURES BY CHROMATOGRAPHY

As indicated in the previous section, each chromatographic zone may be contaminated with traces of the less absorbed constituents that precede it. By contrast, each zone is usually entirely free of all the more absorbed constituents that follow it. Only the least absorbed constituent is absolutely free of all the other components of the mixture.

In studies of the carotenoid and chlorophyll pigments of algae, reversal of the migration sequence was frequently utilized in order to free a pigment of the traces of less adsorbed colored substances with which it was contaminated. This reversal of sequences was usually obtained by readsorption with variation of the solvent or the adsorbent. With mixtures of several pigments, however, this procedure could not be employed systematically, because there were few combinations of solvents and adsorbents that permitted each pigment to form the least adsorbed

zone, and these could be discovered only on the basis of empirical investigation.

Now it appears that systematic, absolute separations of mixtures are possible. This may be accomplished when the primary separation is performed with two immiscible liquids as the chromatographic system.

If one liquid, *A*, is made the fixed phase, as in a gel, and if a second liquid, *B*, is made the mobile wash liquid, then four solutes, *W*, *X*, *Y*, and *Z*, may separate in this sequence as indicated in Table II. If liquid *B* is immobilized and *A* is the wash liquid, the solutes will separate in the reverse sequence as indicated in the table (*57*, *193*, *265*, *335*, *377*). If the mixture is separated in a column with *A* fixed and *B* mobile, *Z* will be obtained free of the more absorbed *W*, *X*, and *Y*. *Y* will be free of *W* and *X*, but it will be contaminated by traces of *Z*; hence it is readsorbed with *B* fixed and *A* mobile, so that it is obtained free of *Z*. Similarly, *X* is obtained from the first system free of *W*, but it is contaminated with traces of *Y* and *Z*; hence it is reabsorbed with *B* fixed and *A* mobile, whereupon it is obtained free of the now more absorbed *Z* and *Y*. By reabsorption *W* is also obtained entirely free of *X*, *Y*, and *Z*.

This systematic procedure should be applicable to mixtures regardless of the number of the components. It is not applicable with chromatographic systems in which one of the phases is a solid or a gas, as such phases cannot be reversed.

Table II. Sequences of Solutes *W*, *X*, *Y*, and *Z* When Liquids *A* and *B* Are Made Alternately Mobile Phase and Wash Liquid

Fixed liquid	*A*	*B*
Wash liquid	*B*	*A*
Sequences of *W*, *X*, *Y*, and *Z*	*W*	*Z*
	X	*Y*
	Y	*X*
	Z	*W*

CHROMATOGRAPHY BY ADSORPTION

Absorbents (*135*) of various specificity (*44*, *111*, *212*, *323*, *383*) have been widely employed in columns, and with various methods of detection (*24*, *34*), for the resolution of mixtures. Examples are starch for amino acids (*13*), Celite for derivatives of amino acids (*270*) and for organic acids (*356*), wool for enantiomorphic acids (*37*, *99*), silica gel for organic acids (*95*, *228*, *234*, *260*, *356*, *382*) and for organic bases (*314*), bone char (*18*) and cellulose (*60*) for sugars, calcium phosphate for proteins (*345*), clay for sugars (*29*), various absorbents for dyes and terpenes (*284*, *370*) and for carotenoids (*9*, *11*, *78*, *104*, *113*, *121*, *139*, *166–170*), glucosides (*2*, *334*), anthocyanidin (*325*), sex hormones (*10*, *16*, *17*), nucleic acids (*383*), phosphorylated substances (*23*, *94*), hydrocarbons (*138*, *145*), alcohols (*255*), lecithin (*289*), vitamins (*124*, *281*), and wines (*236*). Columnar absorption has been employed for the examination of urine, including the detection of gentisic acid (*256*), porphyrins (*258*), hydroxytyramine (*92*), and ionone oxidation products (*279*). Celite serves for the fractionation of cytoplasmic components (*293*, *294*).

Columnar methods have been utilized for the isolation of several inorganic substances. Examples are silicic acid for nitrogen oxides (*102*) and for hafnium (*26*), charcoal for plutonium (*61*), cellulose for zinc (*31*), a combination of absorption and elution for radium and barium (*351*), and adsorption on alumina for isolation of cobalt as nitroso R salt complex (*75*).

ION EXCHANGE

Research is continuing on the preparation of new resins with modified properties (*27*, *374*). An interesting variation is the chemical treatment of cotton to yield ion exchange properties (*157*). The theory of exchange phenomena is being advanced through the study of exchange affinity, rates, and equilibria on both old and new resins (*36*, *58*, *144*, *238*, *286*, *291*). An important development is the use of ion exchangers for determining activity coefficients of ions in solution (*66*, *316*).

The most spectacular growth in the use of ion exchange materials is in the field of biochemistry. Ion exchange chromatography has been applied to the study of proteins (*150*, *288*), nucleic acids and nucleotides (*65*, *156*, *187*, *233*, *257*, *320*, *362*), amino acids (*40*, *86*, *246*, *266*, *305*, *306*, *376*), other organic acids (*46*, *271*), enzymes (*59*), extracts of liver (*52*), flavanoids (*110*), cellulose xanthate (*303*), and nicotinamide (*171*). Of particular interest in organic chemistry is the use of anion exchange resins with borate complexing agents. These agents form complexes with polyalcohols such as glycerol (*381*) and sugars (*183*) and hence serve for their separation by ion exchange chromatography.

Several recent papers deal with the use of anion exchangers for the separation of inorganic salts. In hydrochloric-hydrofluoric acid mixtures, niobium, tantalum, and protactinium can be separated through their exchange sorption as anions (*189*, *190*). A basis is also provided for the separation of iron(III) from aluminum, chromium, and the rare earths by virtue of its anion sorption in strong hydrochloric acid (*248*). Solutes such as hydrochloric acid, lithium chloride, cobalt chloride, cobalt nitrate, cupric chloride, and nickel nitrate are reported to sorb on the anion exchange resin Dowex A-1 as molecules from solution in acetone (*172*).

Rare earth separations continue to dominate the literature in the field of inorganic chemistry (*142*, *148*, *149*, *182*, *239*, *326*, *327*). Separations of zirconium and hafnium (*154*, *218*, *340*), carrier-free thorium 234 (*83*), titanium and iron (*380*), and seventh group anions (*12*) are also reported.

For large scale continuous operation, moving ion exchange beds have been developed (*143*). Ion exchangers are used in the treatment of radioactive wastes (*14*).

While some fractionation of isotopes can be effected through the use of ion exchangers, on the whole the method does not appear promising (*128*); nevertheless, continuous methods for isotope enrichment have been designed (*77*).

Ion exchange for deionization purposes (*197*, *227*) has been extended to the purification of beet sugar (*237*) and of glycerol (*342*).

PAPER CHROMATOGRAPHY

Not only are the absorptive properties of various papers (*300*) utilized for the separation of mixtures, but the paper is often impregnated with solids and liquids which then serve as the sorptive phase, both by chemical reaction and by liquid-liquid partition. An enormous variety of solvents has been employed as the mobile phase, and many more have yet to be tested. The effectiveness of the several solvents must be evaluated in terms of the chromatographic system itself (*232*). As the possibility for variation is enormous, no attempt has been made to classify the solvents (*13*, *21*, *98*, *225*, *354*).

In many investigations, the R_F values of solutes in paper have been reported without reference to the temperature, the concentration, the pH (*159*), or the composition (*50*) of the solution or of the wash liquid (*21*). Now, however, all these conditions have been found to affect the migration rates (*21*); hence they should be reported along with the *R* values (*49*, *50*, *232*). Indeed with aromatic and amino acids, the variation of migration rates with variation of pH may be utilized to improve the separability (*5*, *71*, *98*, *225*).

The kinetics of paper chromatography are similar to those of column chromatography (*250*). The operation of paper chromatography is more versatile, however, as strips, strings (*358*), disks, and sheets of cellulose fiber may be used (*174*, *217*, *250*, *278*, *349*, *358*), on a very small scale (*358*), on a preparative scale (*278*) as with many spots (*74*, *217*), and on a large scale (*140*) as by use of cellulose (*60*) or paper in columns (*385*). Separations may be improved by transverse development with a second solvent (two-way chromatography), and they may be

observed by various physical (*45, 147, 232, 249, 250, 366, 378*) and chemical methods (*48, 73, 103, 349*).

Paper chromatography has been utilized for the separation of mixtures of monocarboxylic and of dicarboxylic acids (*42, 155, 177, 219, 262, 331, 359*), of aromatic acids (*98*), of hydroxy and keto acids (*216*), of ketohexonic acids (*203*), and of 2,4-dinitrophenylhydrazones of keto acids (*5, 71*).

A large number of investigations pertain to the detection (*277*), isolation, identification, and estimation (*33, 202, 261, 269*) of amino acids. These reports include the effects of various solvents (*21, 32, 47, 50, 225*), acid (*159*), temperature (*49*), various reagents such as ninhydrin and permanganate (*73, 103, 114, 175, 269*), large scale separations as multiple spots (*140*), and the destruction of the amino acids (*45, 261*) and their preservation (*175*). Paper serves for detection of amino acids in the effluent from columns (*13*) and for detection of gamma-amino butyric acid (*13, 297, 354*), threonine and homoserine (*100*) and amino acids of tea leaf (*296*), microorganisms (*221, 355*), and ACTH (*215*). Amino acids formed by enzymatic decarboxylation of dicarboxylic acids (*240, 298*), by enzymatic and acid hydrolysis of proteins (*215, 360, 379*), and by transamination (*97, 109*) were likewise separated in paper. The 2,4-dinitrophenyl derivatives of amino acids were also separable (*32, 181*).

Many sugars have been separated (*161*), detected (*20, 48*), and estimated (*226*) by paper chromatography. The R_F values are inversely proportional to the melting points (*158*). Paper serves for the examination of sugars from various natural sources (*15, 85, 93, 105, 180*), for separation of various phosphorylated sugars (*213, 318, 363*), and for isolation of the 2,4-dinitrophenylhydrazones of decomposed sugars (*188, 267*).

Paper chromatography has been utilized for the investigation of various biological products. Examples are adrenaline (*115, 309*), alkaloids (*56*), antibiotics (*321, 358*), ascorbic acid (*282, 372*), glucosides (*311*), nicotinic acid (*186*), histamine (*230*), peptides (*215*), polyphenols (*295*), porphyrins (*259*), purines (*285*), pteridines (*3*), steroids (*51, 141, 192, 193*), thyroxine (*352*), tryptophan metabolites (*235*), uric acid (*347*), nucleic acids (*28, 232, 324, 365*), and other phosphorylated bases (*25, 361*). Organic substances examined were amines (*39*), azo dyes (*76*), alcohols (*165*), pyridine derivatives (*153*), phenols (*152, 292*), pH indicators (*210*), 2,4-dinitrophenylhydrazones (*290*), sulfonamides (*299*), and water in alcohol (*341*). Racemic 2-naphtholbenzylamine was resolved with phenol as the fixed phase and aqueous *d*-tartaric acid as the mobile phase (*35*).

Many inorganic ions have been separated by paper chromatography (*6, 7, 84, 91, 108, 176, 179, 194, 201, 207, 364*). Methods of detection and systematic procedures for qualitative analysis have also been described (*108, 273–6, 364*).

DIFFERENTIAL MIGRATION BY ELECTROLYSIS

Electrolysis of a solution is accompanied by differential migration of the ions. This selective migration may be observed at the boundaries of a wide zone of a solution placed between two solutions of an electrolyte. The effect is analogous to the migration of the solutes in a wide zone of solution in a chromatographic column. Like break-through analysis, it reveals the migration properties of the ions and the composition of the solution, but it does not resolve the mixture (*8, 89, 132, 133, 146, 200, 205, 214, 247, 313, 330, 348*).

In this moving boundary method, convection and mixing are reduced to a minimum by carrying out the migration at a low temperature near that of the maximum density of water (*8, 200, 214*). The boundaries of the migrating ions are usually located by various optical methods (*200, 214, 220*). The mixture is usually resolved into two or three principal fractions (*132, 133, 328, 332, 346*).

ELECTRICAL MIGRATION FROM A NARROW ZONE IN POROUS MEDIA

The mixing of the zones of migrating solutes has also been controlled through the use of gels such as agar and silicic acid (*122, 123, 268, 322, 357*), and by the use of moist porous solids, such as Celite (*337*), cotton (*337*), cellulose paper (*1, 30, 79–81, 101, 112, 191, 199, 208, 209, 222–224, 242, 243, 245, 264, 268, 308, 312, 317, 338, 339*), glass fiber paper (*338, 339*), glass powder (*129*), and ion exchange resins (*328, 329*) as the migration media. With these media, the ions can be forced to migrate from an initially narrow zone (*209, 337, 357*). Their differential migration yields an extensive resolution of the mixture with formation of discrete zones analogous to those obtained in chromatographic separations (*30, 80, 129, 199, 209, 337, 338*); hence the descriptive name electrochromatography (*206*). This differential electrical migration method, which has been reviewed by Lederer (*209*), is now being utilized in many fields, particularly in studies of amino acids and proteins (*30, 80, 81, 101, 129, 199, 209, 222–224, 242, 243, 245, 264, 268, 312, 317, 328*), of nucleotides (*322*), of cellulose (*1*), and of various inorganic ions (*112, 132, 133, 191, 208, 209, 329, 337–339, 357*).

This electrical separation of ions in porous or gelatinous media may be carried out in tubes or columns (*129, 337*) or in stacks (*112*), strips, or sheets of filter paper (*30, 79–81, 199, 209*). The paper may be suspended between two solutions in a closed vessel (*242*) or draped across a rod between the solutions (*79–81, 101*). It may be stretched horizontally in a closed vessel (*223, 224*), or it may be compressed between panes of glass or plastic (*199, 339*). For the control of temperature, the moist paper protected by glass or plastic may be cooled with water, by immersion in a chlorinated hydrocarbon in a thermostat (*199*), by contact with a metal block (*191*), by operation in a cold room (*199*), or by suspension in a light inert gas in a closed vessel in a thermostat (*222–224*).

Separations by electromigration in paper are especially adaptable, because a narrow zone of the mixture can be added conveniently to the migration cell. The paper may also be examined in many ways in order to locate the separated ions. All the specialized techniques developed in the field of paper chromatography may be employed for this purpose. Moreover, solutes separated in paper may be recovered by the standard elution techniques for further investigation of their properties.

TWO-WAY ELECTROCHROMATOGRAPHY

Ions that are partially separated by one-way migration may be resolved further by variation of the solvent followed by electrical migration in a direction at right angles to the first or one-way migration (*80, 338*). Because of its similarity to two-way chromatography, this latter procedure is known as two-way electromigration, two-way paper electrophoresis, two-way electrochromatography (*338*), and two-dimensional electrophoresis (*80*). It has been applied to the separation of mixtures of various cations (*338*) and amino acids (*80*).

Electrical migration in one direction in one solvent followed by electrical migration in a transverse direction in the same solvent has also been called two-dimensional electrophoresis (*199*). In principle, however, this use is not different from continued electromigration in one direction, although it has the possibility of revealing small differences among the trailing regions of zones, such as those of the serum proteins, that are not revealed by extended one-way migration (*199*). In the future, the careful worker should distinguish between two-way electromigration with different electrolytes and two-way electromigration with the same electrolyte.

ELECTROLYTES AND SEPARABILITY

Solutes, such as the supporting electrolyte, the concentration of the supporting electrolyte, the pH of the solution, and the concentration of the mixture to be resolved are all important

factors in the determination of electrical migration rates. Not only the rate of migration but also the direction of migration and the sequences of migration are functions of the nature and the concentration of the electrolyte. The electromigration rates and sequences, which are especially useful for the detection, isolation, and description of various ions (*199, 209, 338, 339*), must, therefore, be defined in terms of the composition of the electrolyte and the properties of the nonmobile phase. The electromigration rates in various electrolytes bear little relationship to the specific conductances of the ions at infinite dilution.

Complex-forming substances added to the electrolyte often change the sign of the various ions, so that their direction of migration is reversed. This effect provides a convenient method for increasing the selectivity of electromigration as an analytical tool. It may be employed to obtain absolute separations of similar ions such as copper and nickel (*80, 81, 338, 339*).

SOLVENTS AND ELECTRODE REACTIONS

Reactions at the anode and at the cathode produce acidic and basic zones about the respective electrodes. Because of the migration of the anions away from the cathode and of the cations away from the anode, these acid and alkaline zones migrate toward each other and sometimes interfere with the separation of the ions of the mixture (*339*). These electrode effects may be reduced or avoided by the use of a very long migration system, by the use of reversible electrodes (*191*), by the use of weakly dissociated buffers (*338*), by large vessels of the electrolyte placed in contact with the porous media (*199*), by flow of the electrolyte over the electrodes, thereby removing the products of electrolysis, and by the use of agar bridges between the electrode vessels and the migration tubes (*223*). These agar bridges should be prepared from the buffer plus agar and should not contain highly conducting salts, because these may yield acid and basic zones at each end of the agar, especially if the electrolyte is either a weak acid or a weak base.

There is much room for improvement in the development of electrode vessels and in the selection of buffers and electrolytes. These electrolyte solutions must keep the mixtures in solution, they should yield a maximum resolution of the mixture for the electrical current consumed, and they should not yield undesirable products at the electrodes.

ANOMALOUS MIGRATION BEHAVIOR

Electromigration in porous media sometimes varies unpredictably. In a piece of moist paper, the migration of amino acids may be proportional to the time of migration (*223*), whereas with some cations such as cerium, the migration rates may vary with time. With this inorganic ion the rate of change of the migration rates is also subject to variation. With proteins, variations of the migration rates have also been reported (*81*). The reasons for the differences and variations are not clear (*81, 222, 223*).

MECHANISM AND NOMENCLATURE OF ELECTRICAL MIGRATION

In gels and in porous sorptive media, the electrical migration of ions follows a zigzag path (*199*). The migration may also be retarded by combination of the ions with the media (*329, 339*). As a consequence, the migration rates of the ions are much less than those in solutions of the electrolyte (*329*).

Separations effected by differential migration of ions in porous media are known as electrophoresis in paper, paper electrophoresis, paper electrochromatography, paper ionography (*222–224*), electrochromatography (*338, 339*), zone electrophoresis (*129*), and electromigration in ion exchangers (*329*). Ionophoresis and electrophoresis refer, respectively, to the electrical migration of ions and of colloidal particles; hence the distinction between the two terms is not always clear. Electromigration includes both ionophoresis and electrophoresis.

COMBINATIONS OF FORCES FOR DIFFERENTIAL MIGRATION

Most of the differential migration methods of Table I result from the simultaneous action of two or more forces. Three classes of such methods may be distinguished:

1. Forces opposed in the same dimension. Fractional distillation, in which a temperature gradient and gravity are opposed, is an example.
2. Forces at right angles, discontinuous methods. An example of this is the thermogravitational method, in which gravity acts at right angles to a temperature gradient.

In both (1) and (2) the opposed forces lead to a multiplication of simple distribution effects. The methods can be operated batchwise with complete resolution, or continuously, with resolution into but two principal components. They are discussed more fully in the next section.

3. Forces at right angles, continuous methods. When a narrow stream of mixture is acted upon by certain forces at right angles, continuous resolution into all components may be possible. Only two methods of this type have been developed thus far, the mass spectrometer and continuous electrochromatography. The former method applies to all substances capable of being ionized in vacuum, and the latter to all charged substances in solution.

COUNTERCURRENT FRACTIONATING PROCESSES DEPENDENT UPON GRAVITY PLUS OTHER FORCES

A number of fractionating processes depend in part on gravity to effect countercurrent distribution between two phases (or otherwise distinct regions differing in composition and density). Processes of this type which have present or potential importance are:

Fractional distillation
Countercurrent extraction
Countercurrent chemical exchange
Mass diffusion
Thermogravitational processes
Electrogravitational processes

Chromatography is also a countercurrent process in a relative sense, and successful mathematical treatments have been based on this concept (*57*). From this standpoint, other countercurrent processes such as fractional distillation may be compared with the differential migration phenomena of chromatography.

In order to make the analogy between distillation and chromatographic absorption somewhat clearer, one may imagine all the liquid mixture in a narrow zone within a long fractionating column with a thermal gradient and with sufficient holdback to retain all the refluxing fractions. Under these conditions, the mixture should separate into a series of contiguous zones of vapor and liquid, each pair containing a single constituent of the mixture.

Fractional distillation, as ordinarily practiced, is not characterized by movement of a narrow zone of mixture. In the conventional fractionating column, upward flow of the vapor phase is maintained by continuous vaporization in the pot, and downward flow of liquid by condensation and gravity. In an efficient column under total reflux, there is a succession of vapor-liquid equilibria at each "plate," and a vertical concentration gradient is established with the pure, more volatile constituent at the top of the column. When material is taken off at the top, the process can be considered as a differential migration of constituents from the pot through the column. In the terminology of chromatography, the more volatile constituents are successively displaced through the column by the less volatile. Because the liquid phase is returned to the pot, the boundary of the displacing medium is essentially stationary, until all the more volatile constituent is removed. It is this refluxing or countercurrent flow

at the boundary between two phases that distinguishes fractional distillation from the chromatographic separations. By fractional distillation it is possible to separate large quantities of the mixture in a relatively small fractionating column, for most of the mixture remains in the pot. In chromatographic columns, by contrast, the nonmobile phase must hold the entire charge with much space remaining for separations by differential migration. Thus large scale batch separations are more readily handled in a fractionating column than in a chromatographic column of comparable dimensions. Furthermore, the temperature of the refluxing distillate provides an extraordinarily simple method for detection of the several fractions.

The well-known methods of countercurrent extraction (*41, 120, 173, 184, 204, 304, 353, 369*) and chemical exchange (*64*) are closely related to fractional distillation. In both these methods a counter flow of two phases is maintained, with the overall result that a differential migration of constituents occurs. With the apparatus designed by Craig, both these countercurrent methods may be utilized for the extensive resolution of a mixture contained in an initially narrow zone (*19, 68, 70, 126, 134, 310*).

Thermal diffusion has been combined with convection through use of an apparatus commonly referred to as a Clusius column, and the combined effect comprises the thermogravitational method. This process, along with mass diffusion and electrogravitational methods, differs from the other three processes in this section in that countercurrent flow is maintained, not between separate phases but between normally miscible solutions maintained at different concentration and density by a thermal or electrical gradient. A substantial body of literature has grown up around the thermogravitational process, but mass diffusion and the electrogravitational processes are comparative newcomers. Recent literature on thermal diffusion methods includes applications to gas analysis (*373*), the theory of liquid phase separations (*280*), and the theory of isotope separations (*229*).

In mass diffusion (*22*) a mixture of gases diffuses into a vertical layer of vapor (usually steam) which circulates by action of gravity. The vapor is produced continuously at one wall and condensed at another. The gases, having diffused selectively into the layer of vapor, are carried downward, and a continuous vertical distribution of concentration is established. The method has been suggested for certain isotope separations. Closely related to mass diffusion is the method of "sweep" diffusion (*62*).

The method of electrophoresis-convection (*43, 53–55*) is designed for the separation of proteins. The protein mixture is contained in a sac impermeable to the protein, but permeable to small ions. This sac is immersed in a conducting solution (buffered) between two electrodes. On passage of current, all electrolytic reactions occur outside the sac at the electrodes, but within, a horizontal potential gradient is established, which leads to a horizontal concentration gradient of the protein. The density gradient thereby established gives rise to a convection current and concentration of the protein in the bottom of the sac. Different fractions of the protein are sorted out in this process by virtue of their differences in electrophoretic mobility. The degree of fractionation obtained to date is very promising.

Another method, which combines electrolysis, electromigration, and convection, all interrelated, is designed primarily for the concentration and separation of simple electrolytes (*253, 254*). As an example of this method, a solution of a chloride, MCl is placed between two vertical silver–silver chloride electrodes. A combination of the electrode process with electromigration leads to concentration of MCl in the cathode region and depletion in the anode region. The density gradient thereby established leads to a convection current and concentration of electrolyte in the bottom of the cell. As in the electrophoresis-convection method, different cations can be separated because of differences in ion mobility. The method is very effective in exhausting electrolytes from solution, but its efficacy in performing difficult ion separations has not been reported. Some of the elementary effects which are related to this method have been treated theoretically (*272*).

ELECTRICAL MIGRATION PLUS FLOW OF SOLVENT

Discontinuous Separations. With porous media to ensure uniform flow of solvent, flow of electrical current has been combined with transverse flow of solvent in order to effect the separation of mixtures contained in a small zone. The flow of solvent may be upward as by capillary rise in a sheet of paper (*137*) but more frequently it is downward induced by gravity (*80, 339*). The porous media may be powdered glass, various filter aids, paper, or ion exchangers.

This combination of forces may operate when the solutes, such as amino acids and inorganic cations and anions, are very weakly absorbed by the filtration media or when they are strongly absorbed (*339*).

For this discontinuous or batchwise separation, a spot or small zone of the mixture is added to the moist porous medium. Downward displacement of the solutes is caused by chromatography or flow of solvent. Horizontal displacement is caused by electrolysis. The separation of the mixture results in the formation of a series of zones or spots in the porous medium (*137, 339*). As pointed out in last year's review, the flow of solvent may also precede or follow the electrical migration.

Continuous Separations. The separation of mixtures by electromigration plus flow of solvent may be effected continuously by the introduction of a narrow stream of the mixture while both electrolyte and electrical current are flowing through the porous medium (*79, 308, 336, 339, 344*). Under these conditions the several components of the mixture follow separate paths through the medium and emerge at different places where they may be collected continuously in separate portions of the electrolyte. This method permits complete and continuous separations of various anions (*308*), cations (*308*), and proteins (*79*). The porous media may be powdered glass (*344*), special filter paper between glass sheets (*308, 339*), or sheets of filter paper suspended in a closed atmosphere saturated with solvent vapor to prevent evaporation (*79*).

The narrow zone of mixture may be introduced through a special cell (*344*), through a wick of filter paper (*339*), or through a hypodermic needle from a syringe compressed by a screw driven by a synchronous motor (*308*).

In paper employed as a filtration medium, continuous separation of solutes by electromigration plus chromatography depends upon many variable conditions. These conditions, particularly the composition of the electrolyte, affect the sorbability of the ions and their migration in the electrical field. Under some conditions the separation by chromatographic forces may just balance the separation by electromigration, so that two different ions may follow the same path through the electromigration cell but at different rates (*339*). Variation of the electrolyte, as by the addition of solutes that form complexes with the ions, often suffices to make them follow separate paths.

This continuous electromigration method is variously known as continuous electrophoresis (*343*) and continuous electrochromatography (*308*). The apparatus is referred to as continuous electrophoresis cells (*308, 339*), the latter term being preferred to electrographic cells (*339*).

Investigations now in progress indicate that absolute separations of multicomponent mixtures may be possible by the continuous electrochromatographic method. For economical separations, however, much attention must be devoted to the selection of the electrolyte.

SUMMARY

Differential migration produced by various forces and carried out under various conditions provides many sensitive and widely applicable analytical methods. All these methods are based

upon simple principles. Many of them permit the complete resolution of complex mixtures and the recovery of the unaltered constituents. Because great variation of the methods is possible, there are few valid rules for the selection of the best conditions for the resolution of mixtures.

Many of these migration methods are based upon several different properties of the materials to be separated. Some of these properties such as solubility, partition between immiscible phases, density, sign of electrical charge, and electrical mobility, are remotely related to one another. Because of the complexity of this relationship, the prediction of one property in terms of another is impossible in most cases. The selection of the best conditions for the resolution of a mixture is usually a trial and error procedure. Separations ineffective under some conditions may be very effective under slightly different conditions. Although differential migration is common to all these methods, the several techniques supplement one another and permit the resolution of mixtures of many kinds of substances. Differential migration methods constitute a large fraction of all analytical techniques. While newer methods of differential chemical analysis do not necessarily belong under the heading of differential migration (*127*, *211*), there is every reason to believe that the general principles outlined in this paper embrace analogous techniques which remain to be discovered.

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DISTILLATION

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THIS year it is more difficult than usual to choose a single outstanding advance in analytical distillation. Possibly the most significant publications are those dealing with the principles of fractionating column design and operation. These contributions do not provide a complete or specific answer to an analyst's prayers. However, they offer useful information on many small matters, and as a whole they suggest that eventually there will be forthcoming a relatively concise set of principles for analytical fractionation.

The largest single group of papers relating to the principles of analytical fractionation are those of English investigators (*35-37, 55, 56, 64, 65*). Among them, these papers cover the range of subjects from construction details to the elements of mass transfer through the interphase vapor and liquid films in a packed column. The new *Journal of Applied Chemistry* has become required reading for those interested in precise distillation.

GENERAL APPARATUS

Once again, the papers describing complete fractionation units or parts of them are numerous. Automatic control is emphasized in most cases. Dixon and Ronnebeck (*37*) point out the importance of smooth operation and close control of operating variables in difficult separations. They provide automatic controls for adjustment of reflux ratio, changing of distillate receivers, and recording of temperature as well as other operations. Both glass and stainless steel columns have been described by Dixon. Orrick and Gibson (*96*) have developed a metal-plastic apparatus for analytical fractionation of fluorocarbons. Seventy-two-hour distillations without attention by an operator are possible in the French-Barnard (*47*) all-metal apparatus, which is intended for mixtures boiling from 40° to 180° C. Reflux ratio is controlled according to the slope of the boiling point curve. A number of different spinning band and other special columns have been

designed for analysis of specific mixtures, but are of wide application (*43, 81, 122, 132, 147*). The use of gauze brushes on a spinning band is worthy of special note (*92*).

VACUUM AND MICRO DISTILLATION APPARATUS

The schizoid surface ideas of Hickman (*63*) may well be the beginning of a whole group of new developments in vacuum distillation and related fields, not excluding analytical distillation.

Thermal rectification columns have now been described in more detail (*15, 24*). Williamson (*147*) has developed a spinning band column for fractionation of fatty acid esters at 1-mm. pressure. A column of pilot plant size, suitable for vacuum fractionation, is reported by Shulman (*122*).

Vacuum microcolumns for as little as 1 or 2 ml. of liquid sample were suggested by Reed (*107*), Chiu (*29*), and Conolly and Oldham (*31*). LeRoy (*79*) reports on low temperature fractionation of very small gas samples at pressures from 1 to 0.001 mm. of mercury and determines the vapor pressure of as little as 0.06 ml. of gas. An internal metal condenser is used by Erdos (*41*) in a semimicro distillation setup. The evaluation of microcolumns is made more easily possible by the hypodermic needle sampling device of Walsh and Phelps (*141*).

SPECIALIZED APPARATUS

Laboratory continuous distillation apparatus has been suggested by two different groups of workers. One group (*64*) uses an adaptation of an automatic batch distillation apparatus, which is suitable for distillation of carboy quantities of material. Carlson and coworkers (*26*) have described laboratory continuous distillation assemblies, also automatic, for process research. It will be of interest to note whether there is a continuing exploitation of small scale continuous distillation.

A German publication (*131*) mentions novel laboratory distillation apparatus with standardized sections and parts that may be of either glass or metal.

COLUMN ACCESSORIES

A somewhat smaller number of column accessories than usual have been suggested. For the first time, various devices for automatic control of column jacket temperatures have commanded special attention (*37, 65, 143*). However, there are, as yet, no published data to indicate the exact relation between fractionation results and nonadiabaticity, particularly at finite reflux.

Several devices relating to the still pot section of distillation apparatus are worthy of mention. Stage (*130*) controls still heat input through a pair of manometers. Bumping is still a problem. Bragdon (*22*) emphasizes the old standby of a single platinum tetrahedron to eliminate bumping, while Billitzer (*17*) suggests a combined condenser and stirrer. Several rotary and spinning band columns also use a stirrer at the lower end of the rotating member.

Contributions relating to the head end of the column concern devices to permit distillation of normally solid materials (*35*), high capacity condensers (*60*), heating of reflux to vapor temperature (*7*), the usual variety of reflux dividers and controls (*16, 49, 86, 99*), use of mercury flow to carry off distillate at a desired rate (*73*), and automatic control of distillation through refractive index measurements (*76*). Automatic fraction collectors have become more common (*46, 58*).

COLUMN TEST MIXTURES, COLUMN EVALUATION, AND OPERATING VARIABLES

Radioactive tracer elements have been used for analysis in a distillation study by Hughes and Maloney (*67*). Reynolds and Sugimura (*108*), Junge (*72*), and the Anglo-Iranian Oil Co. (*4*) have presented column performance data of the conventional type. Willingham and Sedlak (*148*) have given details regarding the use of pairs of 1,2-, 1,3-, and 1,4-diethylbenzene as test mixtures from 30 to 760 mm. of mercury using refractive index for analysis. Walsh and Phelps (*141*) have improved on a previously described still pot sampling device (*115*) by using a hypodermic needle through a glass capillary side arm of the still pot, and three-way stopcock and syringe above. Hands and Whitt (*56*) propose an empirical method for estimation of column height using reflux rate, viscosity, and packing characteristics. Eshaya (*42*) suggests a correction factor for the effect of pressure drop in calculating theoretical plates in a column.

There has been considerable attention to pressure drop and maximum vapor rates, particularly for subatmospheric pressure distillation. Cannon and Peters (*25*) have made a thorough study with various test mixtures of the relation between flooding velocity, pressure drop, and various packing characteristics, liquid and vapor properties, and column operating conditions. They propose the simple relation that maximum possible mass velocity is proportional to the square root of the product of the liquid density, the molecular weight, and the operating pressure. Lerner and Grove (*78*) have made a somewhat similar study in columns of larger diameter using water and air.

Hands and Whitt (*55*) suggest operation at two thirds the throughput calculated from the equation that maximum throughput in pound-moles per square foot per hour equals one third the square root of the absolute pressure of distillation in millimeters of mercury. Other papers by Hands *et al.* (*57*) give extensive data on pressure drop in columns 2 and 6 inches in diameter.

Cichelli *et al.* (*30*) have published charts and equations relating theoretical plates, reflux ratio, and sharpness of separation expressed as pole height. The first experimental results on the effect of holdup in batch distillation with more than two components indicate that previous results with binary mixtures could be extrapolated (*114*).

REVIEWS AND BOOKS

A considerable fraction of the more important basic contributions on fractional distillation has been assembled in a reprint volume (*53*). Material on both the theory and the practice of all types of laboratory batch distillation has been completely assembled in the volume on distillation (*144*) of the Weissberger series, "Techniques in Organic Chemistry." Both foreign and domestic publications have carried various types of reviews on the theory, scope, and technique of laboratory, analytical, and general precise fractional distillation (*2, 44, 97, 111, 113, 134, 135*). Still another review (*14*) points out the financial significance of proper laboratory facilities for fractional distillation analysis of inlet and other streams, and cites examples of the dollar value of losses from inadequate analysis and consequent improper design and operation. For the sake of completeness, the previous annual reviews in this journal should be mentioned (*62, 112, 140*).

NEW APPLICATIONS OF DISTILLATION IN ANALYSIS

A new application of precise distillation is arising in connection with recovery of the easily lost, very volatile flavoring components of certain food products (*21, 33*). An entirely different use of a distillation process is in what might be termed arc analysis. This form of carrier distillation or codistillation is coming into increasing use for high temperature separation of relatively nonvolatile metallic oxides and elements (*139, 146*).

LOW TEMPERATURE DISTILLATION

The seminar (*94*) on this subject sponsored by the Natural Gasoline Association of America was attended by 140 registrants from 56 companies and 10 states. Discussion included all phases of the subject from precision of results to morale and training of analysts. One school of thought favored manual operation. Podbielniak (*103, 104*) has published new detailed papers on the

techniques and errors of low temperature distillation. This subject also comprises one entire chapter of Weissberger's book (*144*). A paper by Miller (*88*) summarizes and makes critical comments on the outstanding publications in this field in recent years. A patent (*124*) covers apparatus and procedure for measuring vapor pressures of fractions from low temperature distillation analysis. A European paper (*61*) deals with analysis of various types of hydrocarbon gas samples, using an original model Podbielniak column with double spiral, and various simple automatic devices for automatic control. Fractional condensation at low pressures and temperatures is mentioned in several papers (*79, 84, 123*). Use of a single steel column for fractionation of both low boiling and other higher hydrocarbons was worked out by Schneider (*119*). Refrigeration is avoided and the apparatus is operable from 10 mm. of mercury to 45 atmospheres' pressure.

A completely comprehensive discussion of methods of analysis and their results for helium-bearing natural gases has appeared (*3*).

KJELDAHL DETERMINATIONS

While only simple distillation is required for this much-used standard analytical procedure, there are, as usual, a considerable number of new suggestions that relate to distillation. Most of these concern subjects such as development of microchemical apparatus (*59, 80, 83, 90, 121, 150*), or modification for determination of nitrogen in specific materials (*102*). Standard specifications for microchemical apparatus have been recommended (*133*). Pozzi-Escot (*105*) recommends low-pressure distillation to get increased precision by avoiding oxidation of nitrogen and resultant loss of ammonia.

ALCOHOLIC MATERIALS

Westergaard (*145*) determines volatiles—i.e., alcohol—in the waste of a large still by using a small batch column operating at total reflux. Practically all the alcohol concentrates in the head, and with a standardized charge size and column and condenser holdup, a thermometer at the column head gives a simple method of analysis. The procedure is certainly applicable to other kinds of samples. A number of foreign publications deal with specific distillation problems in the analysis of wine (*77, 110*). Bonaterra (*19*) uses repeated distillation and the furfural–sulfuric acid color reaction for determination of higher alcohols.

ANALYSIS OF PETROLEUM AND PETROLEUM FRACTIONS

Publications on low temperature fractional distillation should be noted in this connection. The paper by Lockwood *et al.* (*81*) describes details of a spinning band column for the entire fractional laboratory distillation of a crude up to 650° F. at 1 mm. A spinning auger high vacuum still and a simple flash still are also described in this paper. Two reports have been issued by the evaluation panel of the Institute of Petroleum Standardization Sub-Committee No. 2 on Crude Oil (*68, 69*). Rossini has presented two new summaries of the American Petroleum Institute–National Bureau of Standards work on hydrocarbons in petroleum (*116, 117*). Additional reports on purification, purity, and properties of API–NBS hydrocarbons have appeared (*134*). Numerous U. S. Bureau of Mines reports have dealt with evaluation of individual crudes (*9, 127–129*), as well as more general problems (*125, 126*). Similar work on foreign crudes or fractions has been reported (*75, 89, 93*). Three papers are concerned with determination of olefins in petroleum or its products (*50, 54, 106*). The volatilities of polynuclear hydrocarbons of high molecular weight in simple molecular distillation were found to be three times greater with white oils than with aromatic oils (*39*). Fractional distillation and adsorption were combined in order to characterize the cuts from a high-sulfur cracked distillate (*149*). Adams (*1*) used simple apparatus for determining straight-run aviation gasoline in crudes.

SYNTHETIC FUELS, COAL AND BY-PRODUCTS, AND OIL SHALE

The U. S. Bureau of Mines is carrying on intensive and extensive work on assay and analysis related to oil shale and shale oil products (*23, 33, 34, 66, 132, 136*). This same organization has described the distillation apparatus used for synthetic fuel analysis at the Bruceton station (*43*). A complete analysis of a Diesel fuel (*142*) has been published, using combinations of preliminary fractionation, silica gel adsorption, and refractionation of 75 gallons into 157 fractions in an 80-plate helix-packed column with 8 to 1 reflux at 50 to 150 mm. of mercury.

Basu and Glenn (*12*) have combined chromatography and molecular distillation with reflux in studying the products of the hydrogenation of coal. Golumbic and coworkers (*51*) use a 54-tube Craig countercurrent extraction apparatus in combination with vacuum fractional distillation. A German paper (*120*) gives details on the analysis of phenol mixtures from coal, again using chromatography combined with rectification. Other foreign publications concern low temperature distillation of Spanish lignite (*5, 6*), heat treatment of alpine peranthracites (*100*), and the use of a high boiling naphthalene-free oil as a carrier in determination of naphthalene in tar oils by fractionation in a column 1350 ml. high (*40*).

MISCELLANEOUS APPLICATIONS

As usual, these involve both simple distillation and fractionation. The listing below has been arranged for easy reference to the various individual papers on miscellaneous subjects.

Ambergris. Volatile constituents (*118*).

Amines. Analysis of methylamines, with special reference to products from ammonium salts and aqueous formaldehyde (*8*).

Antimony Trichloride. Distillation of antimony trichloride reagent to eliminate color and impurities (*91*).

Asphalt. Separating asphalt into its chemical constituents (molecular distillation) (*95*).

Bamboo. Dry distillation (*74*).

Boric Acid. Determination in nickel and in zinc electroplating baths (*151*).

Bread. Report on mold inhibitors, propionates (in bread) (*85*).

Cheese. Determination of volatile acids of cheese (by steam distillation) (*87*).

Chlorides. Modification of Bunsen distillation method for iodometric determination of chlorides (*137*).

Coffee. Determination of halogenated hydrocarbons in caffeine-free coffee (*32*).

Fatty Acids. National olive oils. Composition of fatty acids (*27*).

Fatty Acid Derivatives. Spinning-band column for vacuum fractionation of fatty acid esters (*147*).

Fluorocarbons. Low temperature metal distillation column for gaseous corrosive compounds (*96*).

Hafnium-Zirconium. Separation by fractional distillation procedure (*52*).

Hydrocarbons. Boiling-range determination of petroleum ether for extractions (*98*).

Iodine. Use of distillation for isolating trace constituents as applied to determination of protein-bound iodine (*28*).

Oil, Sperm. Molecular distillation of sperm blubber oil (*70*).

Oil, Tall. Composition of tall oil and its distillation products (*48*).

Pectin. Determination of acetyl in pectin (*101*).

Polymers. Rapid molecular distillation method for determination of degree of polymerization (*20*).

Rubber. Distillation of rubber cement (*13*).

Sodium-Aluminum. Determination of sodium in aluminum and its alloys by vacuum distillation (*82*).

Turpentine. Composition of native turpentines from common pine (*10*).

Composition of representative commercial sample of dry-distillation furnace turpentine (*11*).

Vitamin A. Studies on vitamins A, D, and related substances by molecular distillation (whale liver oil) (*71*).

Water. Determination of moisture by distillation (specific products with many references) (*45*).

Determination of small amounts of water (*109*).

Improved apparatus for determining moisture in rubber by distillation with toluene (*138*).

Improved water separator (*18*).

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ION EXCHANGE

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THE application of ion exchange to analytical chemistry has passed the curiosity stage and has reached the stage at which the principle and technique are rapidly becoming firmly established in many aspects of chemical analyses. Procedures have been developed which enable the average analyst to handle the technique with considerable ease and accuracy. The time is rapidly approaching when columns and bottles of ion exchange resins will be common equipment and reagents in most analytical and other research and development laboratories.

REVIEWS

Several investigators have prepared reviews on the use of ion exchange in analytical chemistry, discussing the general applicability of this new technique. Fulterknecht (*22*) has described the general usefulness of ion exchange in the analytical separation of many organic compounds and inorganic ions, and for rapidly separating and isolating radioactive isotopes. Dickel (*20*) has reviewed and developed the theory of isotope separation using ion exchange resins. Other analytical separations have been reviewed by Buser (*9*), Honda (*29*), Klement (*40*), Schubert (*63*), Tompkins (*75*), and Wickbold (*80–82*). General review articles on the use of ion exchange resins in chromatography have been written by Davies (*17*) and Stein and Moore (*72*).

THEORY

The theoretical studies of Sillen and his coworkers (*68–70*) and Glueckauf and Duncan (*24*) should be of considerable interest to investigators studying the theory of the ion exchange separation of ions on chromatographic columns. Their conclusions and derivations should prove very useful in the interpretation of the chromatographic separations on ion exchange beds.

DETERMINATION OF TOTAL CONCENTRATION

Further studies have been made on the determination of the total concentration of salt solutions by passing the solution through a column of a sulfonic acid cation exchange resin in the hydrogen form. Klyachko (*41*) and Martin (*48*) have found the method to be subject to error for certain salts and under certain conditions and recommend the use of suitable blank determinations and the investigation of the method on salts that have not been previously studied. MacNevin, Riley, and Sweet (*46*), Orlova (*54*), Robertson and Nielson (*59*), and Wickbold (*80*), however, have found the method to be satisfactory for sulfates, natural waters, and other salt solutions.

INORGANIC SEPARATIONS

One of the more important applications of ion exchange in analytical chemistry has been the separation of the various ele-

ments from one another. Studies that have been conducted during the past year illustrate the widespread applicability of this technique to the separation of various elements for the determination of the individual elements and to the removal of an interfering element. Buser (*10*), Kayas (*37*), and Wickbold (*79, 82*) have studied the chromatographic separation of the alkali ions on several cation exchange resins. Wickbold (*79*) has also studied the separation of cadmium and zinc in chloride solutions. Tompkins (*75*) describes a method for the separation of radium and barium on a cation exchange column, employing a citrate developing solution. By imposing an electric potential across an ion exchange column, Natsume and Yasima (*51*) have completely separated cobalt and copper. The separation of iron from aluminum and titanium has been reported by Teicher and Gordon (*74*) and Yoshino and Kojima (*84*). The separation of lanthanum and actinium on a cation exchange resin using ammonium citrate as the developer has been described by Jeng-Tsong (*34*). Although complete separations of hafnium and zirconium have not been achieved by the use of ion exchange techniques, the results obtained by Huffman and Lilly (*30, 31*) and Kraus and Moore (*43, 44*) are of considerable interest. Niobium, tantalum, and protactinium have been separated on anion exchange resins by Kraus and Moore (*42–45*) and Jeng-Tsong (*33*). Separations on an anion exchange resin involving elements of the seventh group of the periodic system have been studied by Atteberry and Boyd (*5*) and Alexander (*3*). The behavior of vanadium on a cation exchange resin has been investigated by Kakihana (*35*).

Further ion exchange chromatographic separations of the rare earths have been made by Butement (*11*), Fitch and Russell (*21*), Higgins and Street (*27*), Ketelle and Boyd (*38*), Matheson (*49*), Spedding and Dye (*73*), and Van der Heijde and Aten (*77*).

The usefulness of ion exchange techniques in removing interfering substances has been demonstrated by Dean (*19*), Gabrielson and Samuelson (*23*), Golovati (*25*), Pratt (*58*), Samuelson (*61*), and Shimizu (*67*).

ORGANIC SEPARATIONS

The importance of ion exchange in analytical chemistry may be readily noted by the remarkable success the technique has achieved in the separation and analysis of ionic organic substances, and in particular, the biologically active compounds. The most spectacular advances have been made in the chromatographic separation of nucleic acid and related compounds. Abrams (*1, 2*), Cohn (*13*), Cohn and Carter (*14*), Hirs, Stein, and Moore (*28*), Sinsheimer and Koerner (*71*), Totter, Volkin, and Carter (*76*), and Volkin and Carter (*78*) have all made excellent contributions in this field. The use of ion exchange resins in the analytical separation of amino acids has been studied further by Davies *et al.* (*17, 18*), Partridge and Brimley (*55, 56*), Boulanger and Biserte (*7*), and Dalgliestl *et al.* (*16*). Nishio (*52*), Kato and Shimizu (*36*), and Novelli and Schmetz (*53*) have incorporated ion exchange techniques in the analysis of vitamins. Other organic separations and analyses include antibiotics (*60*), monosaccharides (*39*), aldehydes and ketones (*23*), gelatin (*32*), pectins (*4*), organic acids (*8, 47, 83*), and cellulose (*62*).

MISCELLANEOUS

The determination and study of activity coefficients by means of ion exchange resins have been investigated by Connick and Mayer (*15*), Schubert (*63, 64*), and Mayer and Schwartz (*50*). Similar studies have been conducted on the use of ion exchange resins in evaluating the nature of various complexes in solutions. Schubert and Lindenbaum (*65*) have measured the equilibrium constants of calcium citrate and related acids, Bosse (*6*) has studied tannin complexes, and Gustavson (*26*) has attempted an elucidation of the phthalatosulfate-chromium complexes using ion exchange resins. Several student experiments demonstrating the principles of ion exchange have been proposed by Castka and Crane (*12*), Peterson (*57*), and Schuler, Boyd, and Kay (*66*).

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EXTRACTION

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THE increased number of reviews dealing with extraction which have appeared during the past year are indicative of the growth of interest in the subject (*22, 38, 47, 52, 61, 85, 92*).

In spite of the greatly increased interest in analytical extraction as a laboratory tool, the contributions on the subject for the past year have not brought forth startling results. They have rather indicated only a steady improvement in apparatus and the general understanding of the subject as a whole. Each year there is a steady improvement in the quality and availability of the solvents required. On the other hand, there has not been a general improvement in the understanding of the factors required in order to choose or compound a highly selective system for any given separation. Unfortunately, with our present understanding, the choosing of a system for difficult separations still requires much experimentation and effort. As literally hundreds of solvent combinations are possible, weeks of careful experimentation may be required to find a system giving sufficient selectivity for the purpose. The problem would now appear to overshadow by far any other which concerns extraction.

In last year's review (*22*) the most important factors to be considered in choosing a satisfactory system were discussed. These still hold for the newer apparatus discussed in this review, except possibly for the completely automatic countercurrent distribution machine (*27*) which is capable of applying thousands of transfers to a given separation. Here a high β value is not so important as a system adhering closely to the law of Nernst, one in which the phases separate quickly, and certain other aspects of a technical nature.

Inability to choose a selective system on theoretical grounds reflects lack of understanding of the phenomena which produce a given partition ratio. The ratio is broadly a measure of the relative attraction or repulsion the competing phases show for the solute. The relative tendency the solute has for associating or forming hydrogen bonds with solvent molecules to form complexes may be a governing factor. At least reasoning along this line helps to bring the absolute K of a given solute within the proper range to be useful, but it does not throw much light on the more subtle requirements that produce a high β value for a given binary mixture.

In general, if the components of a given binary mixture differ considerably in structure and the first suitable solvent tried gives by chance a poor β value, a change to a different solvent combination will give an improved β value. On the other hand, if the two components are similar structurally, such as leucine and isoleucine, the β value is not so easily improved.

In the latter case the search for a system need not be entirely a random trial affair. Early in searches carried out at the Rockefeller Institute for selective systems for the separation of antimalarial bases by countercurrent distribution, buffers (*24*) were found to contribute greatly to selectivity. Furthermore, the optimum buffer concentration, pH, etc., could be quickly established by constructing a plot of concentration or pH against the partition ratio. A system in which the K was sensitive to pH change was usually highly selective. The same approach was used to advantage in the penicillin studies. Golumbic *et al.* (*40*) used a similar approach in their study with phenols.

A graphical approach similar in principle has been employed by Engel *et al.* (*32*) in their search for selective systems to be used in separating estrogens. A four-component system containing water, methanol, chloroform, and carbon tetrachloride seemed of greatest interest. The proportions of the first two were held constant and a plot of K against per cent composition of chloroform–carbon tetrachloride was then enlightening. Certain theoretical deductions from the data were given, which showed the error of considering partition ratios in terms of relative solubilities of the solute in the two phases. This misconception had previously been pointed out by Craig and Craig (*23*) on general grounds.

A large amount of data on liquid-liquid equilibrium for systems of three or more components has now become available and has been listed in the excellent review (*85*) of Treybal. However, it is given in the form most useful for industrial application and not from the analytical viewpoint. Nonetheless, valuable suggestions may be obtained from these data. Saunders (*73*) has made an extensive study of different nitriles as selective solvents for the separation of aromatics from aliphatic petroleum hydrocarbons. He developed several generalizations regarding the most effective type of nitriles.

The mere determination of single partition ratios for solutes in a given system does not alone give sufficient data for choice of the most useful system (see *22*) for separations, but it is one of the first necessary steps. Those interested in a broad survey of partition ratios will find much of interest in the papers of Collander (*19*) in which the effect of changing the structures of the solutes is discussed. In one study the partition ratios of 200 organic compounds in ethyl ether–water are measured and in the other 145 substances in the system isobutyl alcohol–water have been considered. The second system was usually the least selective. This is in line with the generalization that the highest selectivity is to be found in systems whose phases differ most in polarity (*23*). Other considerations, however, make the butanol system a very useful one for separating the more polar solutes, particularly when an automatic countercurrent distribution

apparatus (*27*) with many tubes is available and a certain degree of selectivity can be sacrificed. In homologous series such as the normal fatty acids a β value in the range of 2 to 4 for a CH_2 difference was usually found by Collander. This is of the order shown by the systems developed by Barry *et al.* (*7*) for separating the homologous normal fatty acids. Simple systems of the type studied by Collander were of little use because of nonlinear partition isotherms.

In general, any change in a solute molecule which affects its polarity will strongly affect the partition ratio. This fortunate circumstance together with a countercurrent distribution pattern provides the information required in order to permit unambiguous determination of the molecular weights of larger peptides by assay for the substituting group (*8*). A reagent attacking the free NH_2 groups of the peptide such as the Sanger reagent (2,4-dinitrofluorobenzene) is permitted to react only partially with the peptide under controlled conditions, so that a considerable fraction of unreacted peptide remains. Then a countercurrent distribution pattern determined directly on the reaction mixture will give a series of bands. The monosubstituted band will naturally occur nearest the band of unsubstituted peptide, the disubstituted derivative further removed, and the trisubstituted still further removed. A quantitative analysis for the radical introduced then permits a calculation of molecular weight. The method clearly showed that gramicidin-S is a decapeptide. Attempts to determine its molecular weight by other methods (*82*) had always led to an ambiguous result.

When the molecular weight is derived in this manner the final conclusion is not based on a single measurement but on several fractions throughout the monosubstituted band. These data must also be in agreement with the figure derived from the disubstituted band. Moreover, if the several bands all point to a single molecular weight and the bands are of such shape that impurity is not indicated, the data as a whole give considerable added confidence in the purity of the starting material.

Golumbic and Weller (*41*) have developed a method for accurately measuring large partition ratios and have called it "interchange extraction."

Plattner *et al.* (*68*) have devised a scheme for separating azulenes which is based on differences in their extractability from sulfuric or phosphoric acid by an organic solvent such as carbon tetrachloride, as the acid is progressively diluted with water. It amounts to an elution curve in which a constant volume of water is added to the acid each time an extraction is made. Mathematics for calculating a theoretical elution curve are proposed. The separation of binary mixtures is given.

APPARATUS

To the experimentalist one of the charms of extraction is offered by the great opportunity for the construction and design of new and novel apparatus. Each year brings its new crop. This year several extractors for removal purposes have been reported (*18*, *48*, *80*). Holmes (*50*) described a simple extractor to avoid formation of emulsions. Use of syringes in small scale extraction experiments has been discussed (*10*, *59*). Smith *et al.* (*79*) described a constant temperature separatory funnel for determining liquid-liquid equilibria.

A number of new designs for accomplishing countercurrent distributions have appeared (*27*, *43*, *93*). These operate on the principle of decantation. Tschesche and Könige (*86*) describe a glass spiral type for larger scale work. Lathe and Ruthven (*56*) have described an apparatus which can be rather easily constructed and which possesses a number of advantages; has the disadvantage that the solutions come into contact with polythene tubing. It does not separate the phases by decantation but by permitting the heavier phase to flow slowly through narrow polythene tubing, where a quick tip will cause it to move to the next chamber rather than return to the one from which it came. It has given precise distribution curves.

The investigator who has not had experience with countercurrent distribution will usually approach it as an experiment and try to set up an apparatus for multiple extractions with as little expense and effort as possible. The literature now describes a number of designs with different advantages. However, assembling an extraction train with high numbers of units requires at best a considerable expenditure of time and money. A makeshift arrangement may be the most costly in the end. When the research deals with the separation of unknown and often costly materials, all possible uncertainties should be eliminated at the start. It would therefore seem a mistake to build an apparatus that will not meet the widest possible requirements. The design of cell reported by Craig *et al.* (*27*) incorporates nearly all the features required by countercurrent distribution in its present stage of development. It is more expensive to build than certain other types reported, but well may prove to be the cheapest from the standpoint of the research. This viewpoint becomes much more important when the train is extended to several hundred units and automatic equipment to operate it is added.

For several years it has been obvious that countercurrent distribution would compete more favorably with chromatography for difficult separations were it not for the labor involved in applying high numbers of transfers. The fully automatic countercurrent distribution machine (*27*) goes a long way toward eliminating this shortcoming. It has an automatic filling device for the upper phases and a mechanical robot for putting the apparatus through any choice of movements. A fraction collector for collecting the effluent phases during the single withdrawal procedure is controlled by the robot. A small cocurrent device is attached to the train, which can be used to counteract the effects of phase distortion by higher concentrations of the solute.

When thousands of equilibrium stages are involved, large volumes of solvent are required. This can be overcome in large part by the "recycling" procedure (*27*). Here the effluent tube from the last cell is connected to the O tube, so that the upper phases pass over the lower more than once. This permits the application of several thousand transfers to a mixture of two or three closely related bands with no more solvent required than that needed to fill the machine once. A procedure for making rapid and precise weight analyses (*28*) was developed to meet the need posed by the much larger number of fractions presented by the automatic equipment. A simple rotating evaporator for recovering the residues rapidly and under mild conditions has been described (*26*).

Kies and Davis (*55*) have developed a stage continuous extraction train of simple design. It accomplishes essentially the same effect as the Johnson and Talbot extractor (*51*) or any of the stage continuous extractors when one of the liquid phases is held stationary and the solute is introduced batchwise with the other moving phase [for a review of these extractors see Craig and Craig (*23*, p. 224)]. Kies and Davis suggest the term "cascade distribution process," a very descriptive term. The process is analogous in principle to the "single withdrawal" procedure (*27*) of countercurrent distribution and therefore comparisons should be made on this basis rather than to the less efficient "fundamental" procedure which Kies and Davis chose for comparison.

The novel feature of their extractor lies in the absence of a stirring device to promote the achievement of equilibrium. Instead a diffuser plate of the type familiar in the Kutscher-Steudel type of extractor is used. A wad of glass wool was found to be as effective a diffuser as sintered glass. The extractor should prove very effective for separations involving systems in which solute interchange is very rapid.

The experimental curves showed a degree of deviation from the calculated which could be due to lack of equilibrium or nonlinear partition isotherms. The deviations fortunately favored separation of the binary mixture used as test substances.

Eisenlohr (*31*) has described a new centrifugal countercurrent extractor.

MATHEMATICAL CALCULATIONS AND THEORETICAL CONSIDERATIONS

In extraction the great variations in procedure present just as much of a challenge to the mathematically inclined as the physical operations involved do to the experimentalist. Interest along this line keeps pace with the technical progress and with the general interest in extraction.

Sandell (*72*) has discussed the rationale of analytical extractions. Morrison (*61*) has given a good discussion of the subject.

As regards countercurrent distribution, most of the recent effort has been directed toward more rapid calculation of theoretical curves (*4, 42, 76, 90*). A formula for rapid calculation of single withdrawal curves has been given (*27*).

The relationship of continuous and discontinuous extraction has been treated by Scheibel (*74*). Excellent graphical calculations have also been given by Compere and Ryland (*20*). Kies and Davis (*55*) have presented formulas for calculating curves obtained with their extractor.

The question of the achievement of true equilibrium and the factors which control the rate has always been an interesting one. Solutes and systems vary widely in their rate of approach to equilibrium. The majority of apparatus for both continuous operation and countercurrent distribution has been designed to promote the most rapid approach. In general, amino acids reach equilibrium rapidly, as Felix *et al.* (*33*) found. This may be due to the systems used. The highly charged amino acids exhibit a solubility sufficient for the purpose only in the organic phases of systems in which much water is also present. Here the two phases approach mutual solubility and there apparently is little resistance to the passage of the solute across the interface. However, the fatty acids also were found to approach equilibrium (*7*) very rapidly in isopropyl ether–buffer systems, in spite of the greater differences in polarity of the phases. The penicillins in the same type of system reached equilibrium much more slowly (*6*). Polypeptides with molecular weights of the order of a few thousand apparently reach equilibrium (*25*) in no more time, during a countercurrent distribution, than many solutes of one tenth the size. Even more surprising is the finding that the protein insulin can be fractionated (*44*) almost ideally in the proper system by countercurrent distribution with no extra time allowed for the equilibration period. With these observations in hand it is difficult to believe that rates of diffusion (*75*) can play a very large role in controlling the rates of approach to equilibrium in liquid-liquid systems, at least where there is sufficient agitation for momentary emulsification of the phases. Most countercurrent distribution runs could probably be made with very much shorter equilibration periods.

The larger molecules of interest to biochemistry usually show a marked tendency to associate either with themselves or with other molecules in the solution. They do not behave as ideal solutes. When the association is with like molecules to form dimers, trimers, etc., a nonlinear isotherm results. This type of isotherm is to be avoided if possible when separations are to be made. On the other hand, if the solvent molecules are the ones surrounding the solute molecules to form the complex, the isotherm will be linear. Thus incorporation of sufficient acetic acid into the system (*21*) gives a good approach to linear isotherms with the higher fatty acids, the bile acids (*1*), and certain peptides. At the same time emulsion tendencies are inhibited. Many heterogeneous complexes show sufficient stability (*66*) in the appropriate systems to permit their distribution as ideal solutes. Here there is no dissociation.

A nonlinear partition isotherm produces usually a skewed countercurrent distribution pattern. If several such solutes are present and the objective of the run is separation of all the solutes, there are disadvantages. Either the front or last band, depending on the direction of skewing, can be obtained free of the others very easily with a high percentage recovery but at the expense of the desired result for the other bands.

In the continuous or stage continuous process operated by continuous center feed, such deviations are more serious. These processes are designed usually to separate the mixture into two fractions in a single run. One solute (or family of solutes) moves toward one end of the column and may be called the extract, while the other (or different family), the raffinate, moves in the opposite direction. However, because of the curvature of the nonlinear partition isotherm the solute may at a lower concentration favor the heavier solvent and move in the direction of its flow, but as the concentration builds up the K may shift to favor the lighter solvent. An unpredictable quandary thus arises. When there is such a change of preference of the solute from one phase to the other, the substance has been called a "solutrope" (*78*). A good example of the phenomenon was found by Smith *et al.* (*79*) in the system benzene-pyridine-water.

APPLICATIONS

In the inorganic field separations thus far have involved only simple extraction, even though certain distribution data in the literature indicate that countercurrent distribution would definitely extend the usefulness of the extraction approach. Many separations do not require the countercurrent process. Weinhardt and Hixson (*91*) have found methyl isobutyl ketone to be very selective in preferentially extracting sodium dichromate from an aqueous hydrochloric acid solution containing dichromate and vanadic acid. Separation factors well over 4000 were obtained. They give a short but excellent review of the use of extraction for inorganic separations. In an excellent discussion of the role of extraction in analytical chemistry Morrison (*61*) also gives a review of inorganic separations.

Separation of the rare earths should challenge those interested in extraction. Asselin *et al.* (*3*) have studied the liquid-liquid partition of the rare earth salts from the standpoint of separations. Thorium nitrate could be separated easily from the other nitrates in the system 1-pentanol–aqueous ammonium thiocyanate. The system 1-butanol–water also gave differences. Moeller and Jackson (*60*) have studied the separative extraction of the rare earths in the form of 5,7-dichloro-8-quinolinol chelates. Only fractional separations were achieved by single extractions and obviously a countercurrent process is indicated.

Lithium chloride has been separated from sodium chloride by extraction with butanol (*53*).

An observation of interest has been made by Morton (*62*). He found extraction by butanol of enzyme solutions useful in removing extraneous materials. Such a procedure did not cause denaturation and made further purification much easier.

Countercurrent distribution should prove to be an excellent method of purification of alkaloids. It has already led to the isolation of a number of new alkaloids. Applications have dealt with *Veratrum viride* (*35*), ergot (*45, 46*), wilforine, and wilfordine (*9, 11*). The Brodie methyl orange distribution technique has been applied to the colorimetric determination of alkaloids in tissues (*37*).

In lipide chemistry there is a great need for some tool that will separate the intact materials or slightly modified derivatives. A promising start on fat oxidation products has been made by Zilch and Dutton (*95*) and by Fugger *et al.* (*36*). Introduction of a hydroxyl group into a fat shifts its partition ratio considerably. Improved systems for fatty acid separations have been reported (*7*).

The most striking contribution of countercurrent distribution during the past year has probably been made in the polypeptide field. It has been used by Brink *et al.* in purifying subtilin (*12*), by Brockmann *et al.* in purifying polypeptide antibiotics from *Actinomycetes* (*13–15*), by Payne *et al.* in purification of ACTH (*67*), by du Vigneaud and collaborators on vasopressin (*87*) and oxytocin (*63*), by Felix *et al.* on clupein (*33*), by Velick and Udenfriend in their isotope dilution method (*88*) for amino acid

analysis, and by Kenner (*54*) in purifying synthetic peptide derivatives. Where isolation of amino acids from hydrolyzates is desired, it is a useful tool (*25, 27, 33*). It has settled the question of the purity and molecular weight of gramicidin-S (*8*).

When the problem of the investigation of the metabolic fate of a drug is encountered, countercurrent distribution is rapidly becoming the method of choice. Recent studies along this line include the isolation of a degradation product of folic acid (*69*), of quinoline (*65*), of chloroguanide (*29*), of methadone (*90*), of salicylic acid (*2*), of *p*-aminobenzoic acid (*83*), of tocopherol compounds in feces (*71*), and of the metabolic products formed from the cinchona alkaloids when given to man (*16*).

Flavin and Graff (*34*) have used countercurrent distribution to good advantage in studying the utilization of guanine for nucleic acid biosynthesis by protozoa. The conversion of guanine to adenine was clearly shown.

Engel and collaborators (*32, 77*) continue their excellent work on the separation of estrogens. Separation of sterols should become more interesting with the greatly increased numbers of transfers (*27*) now possible. In spite of the sticky nature of bile, countercurrent distribution has been shown to be an effective tool for separating bile acids both free and conjugated (*1*). Here the higher numbers of transfers were required.

Countercurrent distribution has been of considerable interest in the streptomycin type of antibiotic ever since Titus and Fried (*84*) first showed that the original streptomycin was a mixture of two streptomycins. Such interest continues (*57, 58, 81*).

Rauen and Waldmann (*70*) have studied the separation and characterization of pterins. The most effective system was 1-butanol–0.02 *N* hydrochloric acid. Analysis could be made by the intense fluorescence, which permitted a good run to be made on 30 to 60 micrograms of material. The photo-oxidative degradation was studied with the same technique.

Miscellaneous applications of countercurrent distribution have included interesting studies on the auxins in cabbage (*49*), the methyl substituted anilines (*39*), the purification of sarmentogenin (*17*), the dephosphorylation of nucleotides (*5*), the fractionation of polythene (*30*), and the study of heparin (*94*).

Neuworth *et al.* (*64*) found the Schiebel column to be very effective for removal of tar acids from tar distillates.

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ORGANIC MICROCHEMISTRY

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THE scope of the present review is essentially the same as that of other years. Judged from the number of papers written during the past year, there is no apparent lessening of interest on the part of microchemists in their efforts to improve existing methods of analysis. Noticeable is the increased attention being given both here and abroad to the subject of standardization.

APPARATUS

The accuracy, precision, and utility of the Cornwall syringe, Chaney pipet, and modified tuberculin syringe for delivering from 0.2 to 7.0 ml. of liquid were compared by Dern *et al.* (*29*). They concluded that syringes held the advantage in speed and accuracy and also in adaptability, because other than integral volumes could be measured and viscosity, surface tension, and temperature variations had less effect on the constancy of volumes delivered from syringes than from pipets. British Standards (*16*) specifies the design and dimensions of washout pipets for volumes from 0.1 to 1.0 ml. with tolerance and detailed methods for using the pipets. Flaschka (*41*) has described a combination microburet and Jones reductor which greatly simplifies titrations with solutions that must be kept in an inert atmosphere.

Two new melting point apparatus have been described, one by Hilbck (*61*), the other by Hippenmeyer (*62*). The apparatus of Hilbck uses exchangeable thermometers which increase the accuracy of reading when used over a wide temperature range.

The distillation and sublimation apparatus described by Erdos (*35*) is designed for use under reduced pressure and with small amounts of material. Conolly and Oldham (*27*) also described a distillation apparatus for quantities of 1 ml. or less.

A turntable for carrying out six simultaneous saponifications with reflux condensation was described by Grützner and Hintermaier (*52*). The modified Conway cell designed by Leurquin and Delville (*87*) has three compartments, one for sample, one for reagent, and another for absorbent solution, all covered by a glass plate. The sample and reagent can be mixed without contaminating the absorbent solution. A light, simple bomb for sodium peroxide fusions of micro, semimicro, or macro amounts of starting material was described by Wurzschmitt (*162*). With this bomb ethylene glycol was used in place of potassium nitrate and sugar, as the fusion temperature was lower and the metal of the bomb less affected.

Electrical apparatus described during the past year include a small high temperature, high vacuum furnace by Alberman (*4*), a simple, precise temperature regulator for electric furnaces by Lévy and Schick (*91*), an apparatus for microconductometric titrations of volumes less than 1 ml. by Stock (*135*), and a photoelectric micronephelometer designed for use with 0.1 to 0.5 ml. of solution by Mason (*98*).

Other apparatus included a drying tube described by Bradlow and Vander Werf (*13*), containers and manometers for micromanometric methods by Möhle (*101*), and a device for making pressure precipitation of sulfides by Stock and Heath (*136*).

Balances. Two articles published by Hodsman, one a report on a symposium on microchemical balances (*67*) and the other a discussion of developments in microchemical balance design (*66*), give a comprehensive picture of balance design, materials, and manipulation, as well as the sensitivity, precision, and practical application of results. Brown (*19*) described an improved 5-mg. aluminum foil rider for Ainsworth microbalances which reduced the rider seating errors. Komárek (*80*) discussed the origin of microbalances and Müller (*103*) presented an unpublished paper by Eigenberger in which proposals were made for improving the microlift balance for determining liquid densities. Improvements in the radioactive electronic microbalance were discussed by Feuer (*37*) and several modifications of torsion ultramicrobalances were reported by Korenman *et al.* (*82*). The magnetically controlled quartz fiber microbalance described by Edwards and Baldwin (*34*) had load capacities of 1.2 mg. unbalanced and 100 to 150 mg. balanced with a sensitivity of 0.1 microgram for 6 minutes of arc.

ELEMENTAL ANALYSIS

Carbon and Hydrogen. The determination of carbon and hydrogen in organic compounds continues to be the popular subject of analytical papers; achieving accuracy of analysis with simpler apparatus and technique is usually the goal. Kainz (*75*) has described an apparatus in which nitrous oxides are eliminated in the gravimetric procedure through the use of metallic copper. The advantage claimed for the copper absorbent is that it not only removes the oxides of nitrogen but eliminates the conditioning runs, as it is nonhygroscopic. Belcher and Ingram (*7*) advocate the use of manganese dioxide for the removal of oxides of nitrogen, and using their rapid oxygen flow technique this absorbent can be used outside the combustion tube and at room temperatures. For the slow or conventional combustion method they have described a modified combustion tube packing. The rapid combustion procedure continues to gain in popularity and Ingram (*70*) has described advantages of the rapid combustion process for carbon and hydrogen and outlined methods that have been successfully used in routine analysis. Wagner (*146*) has described a somewhat modified combustion tube which uses readily exchangeable extensions, the one without lead dioxide filling for compounds that do not contain nitrogen and the other with an aged lead dioxide filling for use when nitrogenous organic compounds are burned. He advocates not wiping absorption tubes prior to weighing, a point in accord with methods being adopted in the United States. With increasing interest in organofluorine compounds, it is but natural that studies have been made of methods for the successful analysis of these compounds. Belcher and Goulden (*6*) have proposed a method in

which the sample is burned in a silica combustion tube but in a fairly slow stream of oxygen. The combustion products are further oxidized by passing them over platinum contacts at 750° C. Fluorine together with the other halogens and sulfur is removed by passing over silver wool also at 750° C. Any silicon tetrafluoride that may be formed is removed by granular sodium fluoride kept at 270° C. Reports of preliminary work indicate that fluorocarbons may be analyzed if water vapor is added to the combustion tube. The use of an external absorbent for nitrogen oxides is advocated.

Wurzschmitt (*161*), to avoid possible errors caused by the use of lead dioxide to absorb nitrogen oxides, has suggested the simultaneous determination of nitrogen and hydrogen. The hydrogen, measured as water, is absorbed in a tube placed between the combustion tube and the azotometer.

A statistical study of the factors affecting the accuracy and precision of the carbon and hydrogen microdetermination was reported by Ogg *et al.* (*105*). Treatment of the absorption tubes was the most important factor and the results indicated that the tubes should not be wiped and that the oxygen in the tubes should not be replaced by air. A method for the determination of carbon and hydrogen, based upon a statistical analysis of data obtained from the collaborative study of results from various methods, has been recommended by the referees of the Association of Official Agricultural Chemists as official "first action." The full details of the method are included (*156*). The British, like the Americans, have committees working on the standardization of microchemical apparatus and they have published (*17*) specifications of the component parts of the combustion train, including drawings showing dimensions as well as the quality of the glass and of the rubber tubing.

Several modifications of wet combustion procedures for carbon have been described. One which is applicable for the analysis of 10 to 15 mg. of biological materials, and which yields carbon values with a standard deviation of 1 to 2%, has been described by Hockenhull (*65*).

Charest *et al.* (*24*) have modified the apparatus of the Baker method, omitted potassium iodate from the Van Slyke–Folch reagent, and increased the concentration of chromium trioxide. Using the new apparatus and the modified reagent they have eliminated the cause of high values. A rapid method for the determination of carbon 14 has been described by Harper *et al.* (*54*). This is based upon the method of Entenmann using the Van Slyke–Folch oxidizing reagent. An apparatus is described in which the $C^{14}O_2$ absorption chamber also serves as the filter for the $BaC^{14}O_3$ precipitate. The dried precipitate can be counted with a windowless tube.

Kjeldahl Nitrogen. In the previous review it was noted from work of the authors that there is a minimum critical temperature for the digestion. White and Long (*152*) have proposed conducting the digestion in sealed tubes, which permits very high digestion temperatures and thereby shortens the time for completing the reduction. Jacobs (*72*) has emphasized the necessity of using a minimum of 0.7 to 0.8 gram of potassium sulfate per ml. of sulfuric acid. These amounts are in keeping with the recommended micromethod of the Association of Official Agricultural Chemists.

The popularity of the use of selenium as a catalyst in the digestion continues. Levin *et al.* (*88*) have established 3.5 mg. of selenium to 1 ml. of sulfuric acid as optimum for serum analysis. Ribas and López Capont (*112*) have developed a method using selenium and perchloric acid in the digestion mixture. Marzadro (*97*) has applied the Kjeldahl method to the analysis of compounds containing both ring nitrogen and side-chain nitrogen. The side-chain nitrogen is determined by the Kjeldahl method, the total nitrogen by a modified Dumas method, and the ring nitrogen is obtained by difference.

Sources of errors which can be avoided in the micro-Kjeldahl determination when boric acid is used to trap the ammonia have been shown by Wingo *et al.* (*159*) to be those due to boiling of the distillate prior to titration and "steaming out" the condenser. Stetten's (*133*) study of the acidic behavior of boric acid solutions showed the amount of base required to neutralize boric acid solution of different concentrations to the methyl red end point. Although not a micro study, this paper is pertinent to the micro-Kjeldahl determination of nitrogen when boric acid is used as the ammonia absorbent and indicates the need for adjusting the ammonia–boric acid solution to constant volume before titration. The use of a solution of $NiSO_4(NH_4)_2SO_4.6H_2O$ as the absorbent for ammonia has been advocated by Blom and Schwarz (*10*); as its reaction with ammonia to form amines is rapid and a comparison solution is not necessary, the nickel salt does not interfere with the use of an acid-base indicator.

Several new designs of the Kjeldahl apparatus have been described. Hayazu (*56*) uses dry air instead of steam to sweep the ammonia from the reaction vessel. Leurquin and Delville (*86*) have modified the Van Slyke and Cullen aeration apparatus for the micro-Kjeldahl procedure. Hayazu (*58, 59*) has described a method using the Kjeldahl apparatus for the determination of the nitrite and nitrate ions. A simple distillation apparatus made from a wash bottle, a small-necked flask, absorption flask, and connecting tubes has been described by Möhlau (*100*) for use in the Kjeldahl procedure. Shepard and Jacobs (*127*) have modified the Parnas-Wagner apparatus so that the steam can be diverted from the steam generator without interruption. Klingmüller (*79*) has described an apparatus in which small amounts of ammonia can be distilled in 1 to 1.5 minutes.

Recommended specifications for Kjeldahl flasks, microdigestion rack, manifold, distillation apparatus (both Parnas-Wagner and one-piece model), and an electric steam generator have been published by the Committee on Microchemical Apparatus, Division of Analytical Chemistry, American Chemical Society (*134*).

The referees on microchemical methods, Association of Official Agricultural Chemists, through a statistical analysis of the data obtained by collaborative study of the Kjeldahl method, have recommended a method for adoption as official "first action" by the association (*157*). The investigation included studies of effect of potassium sulfate concentration in the digestion mixture.

Thompson and Morrison (*142*) studied the nesslerization method for determining nitrogen in plant material and determined the effect of such variables as stability of Nessler's solution, temperature and alkalinity effects, and conditions of sample digestion.

Dumas Nitrogen. A modified apparatus for the determination of nitrogen by the Dumas procedure has been described by Dirscherl and Wagner (*32*); the combustion is made in an electric furnace moved with an automatic device. They have also described a modified Kipp generator which they claim will deliver microbubbles even after lengthy periods of idleness.

Specifications for the dimensions of a 1.5-ml. micronitrometer for use with the Dumas combustion train have been established by the British Standards Institute (*18*).

A new method for the determination of nitrogen in organic materials by hydrogenation has been described by Gel'man and Korshun (*45*). The samples are hydrogenated in a rapidly flowing stream of hydrogen in the presence of an iron or nickel catalyst at temperatures of 300° to 400° C. Best results were obtained with the iron catalyst. The evolved ammonia is determined iodometrically with potassium hydrogen iodate and potassium iodide in the absorption liquid and by back-titration with sodium thiosulfate. Through study of the reaction of a mixture of concentrated hydrochloric and nitric acids and monocarboxylated α-monoamines, Renard and Deschamps (*111*) have shown that the volume of gas liberated corresponds to the nitrogen of the organic material according to the equation:

$$R{-}CHNH_2{-}COOH + HCl + HNO_3 \longrightarrow R{-}CHCl{-}COOH + N_2O + 2H_2O$$

Provided the compound studied does not set up secondary

reactions with nitric acid, the proposed method provides a means of determining amine nitrogen of α-amino acids and α-amino sulfonic acids and the amide nitrogen of amides and sulfonamides. Sternglanz *et al.* (*132*) reported a modification and simplification of Zimmermann's Dumas method for nitrogen. Tractable samples were mixed with fine copper oxide in a porcelain boat before being placed in the combustion tube, whereas copper oxide plus cobaltic oxide was used if the material was refractory. Mangeney (*94*) also has described modification of Zimmermann's automatic combustion method for nitrogen in organic compounds. The modified method is equally applicable to micro and semimicro sized samples.

Wurzschmitt (*160*) like other European microanalysts believes that better hydrogen analysis values can be obtained when the hydrogen is determined as a part of the Dumas nitrogen procedure rather than as part of the dry catalytic carbon procedure.

Phosphorus. A titrimetric method for the determination of phosphorus has been described by Sakamoto and Hayazu (*121*). The sample is wet ashed and the phosphorus separated as the molybdate, from which ammonia is evolved by the micro-Kjeldahl procedure. The titer of the standard acid is in terms of phosphorus. Diemair and Baier (*31*) proposed a similar titrimetric procedure which they applied to the determination of phosphorus in growing yeast. Tsuzuki *et al.* (*143*) established a new factor for phosphorus when determined by the micro-Lorenz method of weighing directly the precipitated ammonium phosphomolybdate.

An amperometric titration method for phosphorus has been described by Boos and Conn (*11*) in which the phosphate in the solution of the carbonate fusion products of the phosphorus compound is titrated with 0.1 *M* uranyl acetate at −0.6 volt.

Sterges *et al.* (*131*) have modified the A.O.A.C. official method for phosphorus in plants by adding sulfuric and perchloric acids to the digestion mixture and using the same time for color development in the test sample as for the standard. These changes have shortened the time of analysis and increased the accuracy of the method.

Oxygen. Unterzaucher (*144*) has written a review of experiences gained from 10 years' use of the blank-free iodometric microdetermination of oxygen. The method of Unterzaucher permits the determination of micro, semimicro, and trace quantities of oxygen. For constitutional oxygen 3- to 5-mg. samples are required. The presence of fluorine and phosphorus interferes. The author maintains that his method is characterized by complete freedom from a blank, a view not shared by many American microanalysts. Unterzaucher believes the cause of blanks to be use of impure reagents, inconsistency of temperature of carbon contact, and use of insufficiently cleaned reaction tubes or those whose inner surfaces are damaged. Using this same procedure he has proposed a new method for the determination of carbon and hydrogen. The water from the hydrogen is retained on anhydrous barium chloride, and after the carbon has been determined iodometrically, the oxygen in the water, liberated from the barium chloride, is also determined iodometrically. This method is claimed to give greater accuracy for the carbon and hydrogen than is obtainable by the usual dry-catalytic-oxygen-combustion method. Grant *et al.* (*51*) have made improvements in the iodine pentoxide method for the estimation of carbon monoxide at low concentrations through refinements in the apparatus and by measurement of the liberated iodine spectrophotometrically. Deinum and Schouten (*28*) have described a semimicromethod for the direct determination of oxygen in organic compounds. The details of the method are essentially the same as those described by Unterzaucher.

Sulfur. Walter (*149*) has developed a photometric method for detecting the end point in the titrimetric method for sulfur, using as indicator tetrahydroxyquinone or the alkali salt of rhodizonic acid. Agazzi *et al.* (*3*) and Siegfriedt *et al.* (*128*) both described a small scale oxygen bomb for the determination of sulfur. Agazzi followed the combustion by a gravimetric determination of the sulfate formed, whereas Siegfriedt used the volumetric method employing tetrahydroxyquinone as indicator. A method for the determination of sulfur applicable to all types of organic compounds regardless of the sulfur linkage has been described by Roth (*115*). The sulfur in the compound is oxidized to sulfate in a microbomb tube filled with oxygen. The sulfate is reduced in a formic acid–acetic acid mixture and the hydrogen sulfide is carried by a stream of hydrogen to zinc acetate. The zinc sulfide is converted to hydrogen sulfide, which is determined photometrically from the reduction of methylene blue. For those who are interested in the benzidine method for sulfur determination, Fischer and Sprague (*40*) have shown by means of electron micrographs that the incomplete precipitation of benzidine sulfate in the presence of foreign ions is due to the imperfect crystal formation and growth. A possible explanation of the observed phenomena is based on the Paneth-Fajans-Hahn law. Fischer with Chen (*39*) has also shown that small quantities of sulfate of the order of 0.005 *N* can be determined by direct conductometric titration with standard benzidine dihydrochloride solution. Phosphate ions interfere but can easily be removed.

Hayazu (*57*) and Bussmann (*22*) have described applications of the Zimmermann volumetric sulfur method as well as causes of error that may occur.

A new volumetric method for sulfur has been described by Padowetz (*107*), in which the sulfuric acid produced is precipitated by adding a measured excess of barium chloride and the excess barium chloride is measured by argentometric titration of the chloride ion after the hydrochloric acid formed has been driven off.

An apparatus for the rapid air oxidation of sulfur-containing organic compounds, in which the sample is burned in a tube with an oxidation catalyst packing, has been described by Wilson and Straw (*158*). The catalyst used is vanadium pentoxide on alumina.

A titrimetric method for sulfur, based upon the determination of the amount of barium in excess of that precipitated by the sulfate, in which barium diphenylaminosulfate is used as the indicator and standard Mohr's salt as the titrant to measure the chromate ions in excess of those that react with the excess barium ions, has been described by Tamiya (*138*). Zinneke (*164*) has developed a titrimetric sulfur method in which the organic sulfur compound is burned in a stream of oxygen and the combustion product is passed over hot platinum and then over silver gauze. The latter reacts with the sulfur, forming a coating of silver sulfate. This is dissolved in water and titrated with standard potassium iodide in the presence of nitrite and starch. Sakamoto, Hayazu, and Takenaka (*122*) have advocated the use of wet oxygen in the "dry" catalytic sulfur combustion method.

Rosenberg *et al.* (*114*) have modified the amperometric titration method for sulfhydryl groups. They used a vibrating electrode as a combination electrode and stirrer, and were able to measure amounts of sulfhydryl as small as 1 microgram.

Halogen. A method has been proposed by Gatterer (*43*) for the rapid and reliable determination of chlorine, bromine, iodine, and sulfur. The sample is subjected to a high frequency electromagnetic field and the spectrum is photographed and evaluated in the usual way. Detection is possible down to about 0.001% and quantitative estimation is possible down to 0.1 to 0.033% with an accuracy of 5 to 10%.

The use of sodium peroxide fusions continues to be popular in the determination of halogens. Lévy (*90*) outlines such a method using the Parr bomb for the mineralization of the halogens, which are subsequently determined by his method of potentiometric argentometry by use of equivalence potentials. Martin (*95*) has shown that there is still need for suitable rapid and selective methods for the microchemical determination of the halogens. While he recognizes the advantages of the Parr bomb micromethod for the destruction of organic substances, he calls attention to the fact that exceptionally close maintenance of the experimental

conditions must be observed and that these conditions are yet to be perfected. Agazzi *et al.* (*3*) determined chlorine as well as sulfur in the small scale oxygen bomb described by them. A simplified gravimetric method by which chlorine, bromine, and iodine of organic compounds can be determined has been devised by Safford and Stragand (*118*). The halogen gases, products of dry oxygen-catalytic combustion, are absorbed by a silver gauze. The resulting gain in weight of the gauze by the formation of the silver halides represents directly the halogens of the sample. A potentiometric method for measuring the halogens in a solution of the fusion mixture formed in a Parr bomb has been described by Lévy (*89*). Pääbo and Rottenberg (*106*) have replaced the indirect alkalimetric method of Zacherl and Krainick with a direct mercurimetric titration using diphenylcarbazide as the indicator. The method has been applied to halogenated hydrocarbons and fatty acids. When the sample contains sulfur the results are not satisfactory. A titrimetric method for the simultaneous determination of the halogens and sulfur in catalytic oxidation combustion products has been outlined by Wagner and Bühler (*147*). An argentometric method for the determination of chlorine, bromine, and thiocyanate using a back-titration with potassium iodide and an adsorption indicator of either *p*-ethoxy or *p*-methoxychrysoidine has been suggested by Schulek and Pungor (*126*). Sakaguchi (*120*) has listed eight indicators for the argentometric titration of chlorine, bromine, and iodine and has given the relative sensitivities of each indicator.

The success and failure of the use of the silver–silver chloride electrode for the potentiometric determination of chlorine in biological and nonbiological fluids were discussed by Duxbury (*33*). Viswanathan (*145*) has outlined a titrimetric ultramicroprocedure for the determination of chlorine.

A method for the determination of bromine, in which the bromine in an organic compound is converted to a bromide by heating with metallic sodium and absolute alcohol and the bromide is measured photometrically by the amount of orange-yellow color developed upon the addition of gold chloride, has been described by Desassis and Macheboeuf (*30*). Brandt and Dahlenborg (*15*) have suggested the advantages to be gained by using ultraviolet light when titrating iodine in a two-layer system, acetic acid–water, and chloroform containing thioflavin as the fluorescence indicator. The chloroform solution will not show full fluorescent brilliance until all the iodine has been reduced to iodide.

A method giving excellent results for the determination of iodine in 3- to 4-mg. samples is that of Kainz (*76*), in which the sample is heated with dry potassium, yielding potassium iodide. This is dissolved in water and oxidized with bromine, potassium iodate and iodide are added, and the iodine liberated from the acidified solution is titrated with thiosulfate. Nesh and Peacock (*104*) have used carrier-free radioactive iodine in Baker's method for the determination of protein-bound blood iodine.

The current interest in fluorinated compounds has intensified the need for analytical methods for fluorine analysis. Three papers dealing with this subject have appeared recently. Clark (*26*) has outlined a simple procedure in which the fluorinated organic compound is burned in a stream of oxygen passing over a platinum catalyst in a quartz tube at 900° C. The fluorine is determined by an acid-base titration of the combustion products. Necessary precautions and limitations of the method are discussed. Rickard *et al.* (*113*) have described a method of determining fluorine in solid halocarbons. The sample is decomposed at 1100° C. in a stream of moist oxygen and the fluorine is determined colorimetrically with standard ferric salicyclic acid. The combustion tube can be of quartz, platinized quartz, or platinum. Williams (*154*) is able to detect as little as 1 microgram of fluorine. The halogen is converted to hydrogen fluoride which acts upon glass, silicon from the glass is dissolved, and hydrated silicon dioxide is deposited on the glass by hydrolysis of the silicon tetrafluoride. Optimum conditions are given and a useful apparatus is described.

Other Elements. Kahane and Korach (*74*) described a method for determining selenium in small amounts of seleniferous organic matter. After decomposition by acid digestion the selenium was reduced in a strongly acid medium by sulfur dioxide and weighed as the black selenium.

Mercury was determined by Hirai and Hayazu (*63*) by carrying out a Kjeldahl digestion of the organic matter and then titrating the divalent mercury with thiocyanate by the Volhard method.

Kingsley and Schaffert (*78*) described a method for determining arsenic in samples containing less than 0.1-microgram quantities and discussed the results of applying the method to biological materials.

A micromethod for the boric ion developed by Gautier and Pignard (*44*) depends on the formation of a barium borotartrate complex and can be applied to the determination of boron in inorganic, organic, or biological materials.

A modification of the Lewis-Marmoy method for potassium was reported by Chapman (*23*) for determining potassium in leaf ash. In this volumetric semimicromethod the potassium as the cobaltinitrite in aqueous 30% disodium acid phosphate is titrated with standard permanganate solution.

To ensure that all the ash in a sulfate ash determination exists as the sulfate, Martin (*96*) has suggested that ashing be done as usual in a platinum boat but that ignition be done in a stream of oxygen containing sulfur dioxide gas. The mixture forms sulfuric anhydride in contact with the platinum, which serves as catalyst.

GROUP ANALYSIS

Lithium aluminum hydride was used by Schöniger (*124*) to liberate active hydrogen from 2- to 5-mg. samples. The hydrogen formed was first oxidized to water and the oxygen of the water determined by the Unterzaucher procedure. Schöniger (*123*) described a method for determining unsaturation by catalytic hydrogenation. Ruziczka (*117*) discussed the existing methods for the microdetermination of iodine value and recommended the Gorbach microburet for such determinations. Semimicromethods for both iodine value and saponification number were described by Komori (*81*) using approximately 30 and 100 mg., respectively, of oil or fat. Determination of carbonyl groups with 2,4-dinitrophenylhydrazine was described by Schöniger and Lieb (*125*). Gorbach (*46*) gave directions for determining the carbonyl number of fats with hydrazine hydrochloride using 0.5- to 2.5-mg. samples.

MOLECULAR WEIGHT

A new, less fragile apparatus for determining molecular weights by the isothermal distillation method was described by Hoyer (*68*), who used the apparatus with as little as 0.4 mg. of sample. Hawkins and Arthur (*55*) designed an apparatus which works equally well for determining the molecular weight of both high and low boiling liquids by the vapor density method. According to Brandstätter (*14*), cryoscopic molecular weight determinations can be conducted in preparations placed between the slide and cover glass on the hot-stage microscope. Camphor is too volatile for this method but cyclopentadecanone (Exaltone), bornyl bromide, or camphene may be used.

MOISTURE

Microdetermination of moisture by Karl Fischer titration was the subject of two papers. Wiberley (*153*) described an improved procedure using a special 1-ml. buret and a technique for preserving the reagent so that only weekly standardizations were usually necessary. Ciusa and Moroni (*25*) were skeptical of the feasibility of using Karl Fischer reagent for moisture but state that the method can be recommended for precise microanalyses, if certain precautions are observed.

COMPOUNDS

Sugar. Collaborative results reported by Goss (*49*) showed that Somogyi's micromethod for reducing sugars is satisfactory. Fonty (*42*) recommended the use of polyvinylpyrrolidone or the polyoxyalkylene derivative of sorbitan mono-oleate (Tween 80) to stabilize the suspensions for the Folin-Malmos micromethod for sugar. A review of micromethods for sugar in blood was published by Accoyer (*1*). Small quantities of a mixture of glucose, maltose, and dextrins were analyzed colorimetrically by Rüggeberg (*116*) with an average error of ±4%. Micromethods for serum amylase and blood glucose were described by Teller (*141*) and Accoyer *et al.* (*2*), respectively.

Fatty Acids. Electrometric titration of organic acids was discussed by Ingold (*69*), who used the glass electrode as pH indicator and titration vessel. He recommended the use of tetramethyl ammonium hydroxide in place of alkali hydroxides and glycol monomethyl ether as solvent for non-water-soluble materials. Microtitrations of fatty acid in a mixture of chloroform, ether, and alcohol as solvent were reported by Gracián Tous and Vioque Pizarro (*50*) with errors of about 5% for 5-mg. samples. The microchemical determination of the amino acids in proteins using only 200 to 300 mg. of sample was described by Gorbach (*48*). The analysis requires about 13 hours and includes all recognized essential amino acids. The analysis of certain amino acids separated by paper chromatography was described by Pereira and Serra (*110*). Other methods for organic acids include one for lactic acid by Lang and Pfleger (*85*), two for citric acid by Taussky (*140*) and Buffa (*20*), and a method for picric acid in picrates of organic bases by Stöhr and Scheibl (*137*). A review of the micromethods for *p*-aminosalicylic acid with detailed procedures was published by Stelt (*130*).

Miscellaneous. The colorimetric determination of ethyl alcohol in amounts as low as 1 microgram in 1 ml. of solution was reported by Williams and Reese (*155*). The amount of dichromate consumed in the oxidation of the alcohol was measured by determining the excess dichromate after complexing with *s*-diphenyl carbazide. The 8-quinolinol complex of vanadium was used by Buscarons *et al.* (*21*) to determine alcohols in either organic or aqueous solution.

Free formaldehyde was determined on a micro scale by a spectrophotometric procedure developed by Tanenbaum and Bricker (*139*) employing the time-sensitive reaction between the aldehyde, phenylhydrazine, and potassium ferricyanide. The determination of formaldehyde with chromotropic acid was used by Lambert and Neish (*84*) as a means of determining glycerol in fermentation solutions after the latter had been oxidized with periodic acid. Bradbury (*12*) determined glycerol by reacting it with hydriodic acid to liberate iodine, which finally is determined by thiosulfate titration. Andrade and Suárez (*5*) compared three different methods for determining glycerol and other polyalcohols separately and in mixtures with ethanol, glycol, and sugars. Three pairs of workers—Hirt and Gisclard (*64*), Gunther and Blinn (*53*), and Ketelaar and Hellingman (*77*)—reported methods for determining the insecticide parathion, now being used extensively. A micromethod for the determination of fat reported by Jones (*73*) makes use of the formation of monolayer films and measurement of their areas.

REVIEWS AND GENERAL PAPERS

The fifteen or more general papers and reviews show that this has been a year for summing up, both in the general field of microchemistry and in special fields of application. A review by Benedetti-Pichler (*8*) covered both organic and inorganic microchemistry in the United States, while that by Zacherl (*163*) discussed the situation of microchemistry in Austria. Hecht (*60*) attempted to deduce the trend in microchemistry from the nature of the lectures presented at the 1950 International Microchemical Congress.

Parks and Lykken (*109*) discussed reduced-scale (micro and semimicro) methods of analysis for most of the determinations commonly made in organic analysis. They also reviewed (*108*) the potentiometric, amperometric, and polarographic methods of microanalysis.

The role of microchemistry in the field of biochemistry was discussed by Ley (*92*) including physical instruments, chemical (Pregl) methods, and manometric (Warburg) methods. Microchemistry in practical pharmacy was the subject of an article in which Lüdy-Tenger (*93*) discussed both physical and chemical tests he has found useful. Gorbach (*47*) discussed the application of microchemistry to the fat field and Waldmann (*148*) considered the determination of vitamins as a microchemical problem.

The elemental analysis of nitrogen-containing organic compounds was the subject of a review by Moelants (*102*), in which he considered the various combustion methods. Ishizaka (*71*) reviewed microdiffusion analysis by the Conway method, while Sakaguchi (*119*) discussed the use of organic reagents in microanalysis.

Other general articles bearing on microchemistry were the role of microchemistry in the new fields of analytical chemistry by Wenger (*150*), microchemical applications of catalytic and induced reactions by West (*151*), and a general discussion of spot test analysis by Feigl and West (*36*).

A discussion of the points and problems involved in attempting to reduce the scale of an analytical reaction was presented by Benedetti-Pichler (*9*). Although not specifically for microchemistry, the tables showing the percentage compositions of organic compounds arranged by Kuffner and Gruber (*83*) should be an aid to microanalysts.

Sobotka (*129*) pointed out that the greatest need in microchemistry was a systematic development of micromethods for determining physical constants. The microdetermination of critical mixing temperatures observed on a Kofler hot stage was used by Fischer (*38*) to identify, test the purity of, and quantitatively determine organic liquids. He also listed the different physical micromethods used for liquid examination on the hot stage. Milazzo and Paoloni (*99*) found *o*-dianisidine an effective redox indicator for microtitrations.

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INORGANIC MICROCHEMISTRY

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THE present review is based on articles abstracted in *Chemical Abstracts* and *British Abstracts* during the past year. The scope of the review remains the same as that of last year (*368*), and the reader is referred to accompanying reviews on chromatography, microscopy, nucleonics, fluorometry, polarography, and spectroscopy for correlative information.

Probably the most significant developments in inorganic microchemistry lie in the field of electrometric techniques. The extreme sensitivity of coulometric methods will undoubtedly influence the progress of titrimetric analysis, as will the use of high frequency oscillators, because sensitivity to concentration changes at extremely high dilution will permit significant simplification of present titrimetric procedures. Oscillographic polarography employing platinum electrodes is a promising microchemical tool, and the studies of microelectrodeposition methods should be followed closely.

A very interesting and significant trend is apparent in the chemical aspects of microchemistry, where it is now realized by many investigators that reagents are not all-important. Rather, it is the reaction that is significant—proper conditioning can produce very satisfactory procedures from general reagents that have little selectivity when used directly.

A lack of interest in the use of bioassay methods is apparent. This is unfortunate, and it should prove very profitable for investigators to consider such methods when faced with the problem of estimating extremely small amounts of inorganic materials.

Methods of separation are of recognized importance and have been the subject of many interesting studies. Inorganic chromatography is being widely studied and increased interest is shown in extraction methods.

REVIEWS

Reviews and general surveys of microchemistry and microchemical methods include the annual review of inorganic microchemistry (*368*), the suggestions of Benedetti-Pichler (*32*) for the development of microchemical methods, and a summary of the status of microchemistry in Austria by Zacherl (*391*). The applications of microchemical methods have been discussed by various authors (*129, 268, 338, 341, 367*). Microchemical qualitative methods were reviewed (*60, 166, 255, 258, 294*) and the possibilities of quantitative inorganic semimicromethods for instructional purposes were summarized by Rulfs (*301*).

Vandenbosch discussed (*358*) the value of polarography in microchemistry, colorimetric methods of trace analysis were reviewed by Jones (*176*), Sakaguchi considered the microchemical importance of organic reagents (*305*), West discussed the microchemical applications of catalyzed and induced reactions (*369*), and Feigl and West reviewed (*101*) the state and outlook of spot-test methods.

APPARATUS

Steady progress is evidenced in the development of microchemical apparatus. Standardization is of obvious importance and is being studied in both Europe and the United States; the present status of standardization in this country was discussed by Alber (*3*). The most significant developments are logically in the construction of improved balances and a number of papers deal with the history (*187*), maintenance (*385*), and construction of various types (*88, 167, 188*) of balances. Electromagnetically controlled microbalances are very promising (*86, 235*) and the improved radioactive electronic balance (*103*) should find wide application because of its usefulness in measuring small differences (1 microgram and less) in objects weighing as much as 20 grams. Hodsman's discussion and report on microchemical balance design are of interest (*157, 158*).

Various modifications of pipets and burets have been described (*48, 49*), and Buck and coworkers have suggested a calibration procedure for checking pipets and burets based on a real measurement of delivered droplets of dye (*50*). Miscellaneous microchemical devices include a low-power micromanipulator (*19*), a microdistillation and microsublimation apparatus (*93*), stirrers (*336*), sulfide generators (*337*), reductor buret (*108*), self-sucking capillary siphon (*345*), and a very useful extraction pipet (*61*).

Flame spectrophotometry is a part of the broad field of spectroscopy, but warrants special attention here because of its value in certain microchemical determinations, particularly those of the alkali and alkaline earth metals. Flame photometers have been described by Fox (*112*) and Wilberg (*379*) and a flame-photometer attachment for the spectrograph has been proposed by Schrenk and Smith (*311*).

Table I. Methods of Separation

Subject	Operation	Reference
Mg	Separation (from Na and K) by coprecipitation with $Ag_2O.xH_2O$	(*357*)
	Chromatography	(*85*)
As	Gathered by means of $MnO_2.H_2O$	(*387*)
	Chromatography	(*202*)
Sb	Complexation with tartrate	(*161*)
	Chromatography	(*202*)
Rh	Extraction of triphenylbenzylphosphonium salt	(*350, 351*)
Sn	Extraction of Sn (II and IV) fluorides with Et_2O	(*180*)
	Complexation with tartrate	(*161*)
	Chromatography	(*202, 273*)
U	Precipitation with protein	(*124*)
	Extraction of $UO_2(NO_3)_2$ with Et_2O	(*289*)
	Extraction of cupferrate with CH_3Cl_3	(*22*)
	Complexation by means of fluoride	(*131*)
	Chromatography	(*8*)
Se	Distillation with $HBr-Br_2$	(*213*)
Te	Coprecipitation with Se as gathering agent	(*213*)
Ti	Extraction of 5,7-dibromo-8-hydroxyquinolates with benzene	(*195*)
	Complexation with tartrate	(*161*)
	Chromatography	(*197, 388*)
Mn	Precipitation using $Mg(OH)_2$ as gathering agent	(*94*)
Ca	Chromatography	(*85*)
Ba	Coprecipitation with PbSO	(*64*)
	Chromatography	(*85*)
Sr	Chromatography	(*27, 116*)
K	Chromatography	(*27, 116*)
Bi	Chromatography	(*56*)
Cd	Chromatography	(*56, 202*)
Fe	Pptn. with pyridine (separation from Ni, Co, Zn, Cd, Cu)	(*17*)
	Pptn. with cupferron [separation from Al, Be, Cr, P, B, Mn, Co, Ni, Zn, U (VI)]	(*17*)
	Extraction of $FeCl_3$ with ethers (separation)	(*17, 58, 221, 361*)
	Extraction of cupferrates using $CHCl_3$	(*58*)
	Complexation with tartrate	(*161*)
	Complexation with phosphate or fluoride	(*66, 131, 309, 373*)
	Chromatography	(*5, 56, 388*)
Ni	Extraction of 1,2-cycloheptanedionedioxime complex with CCl_4	(*58*)
	Complexation by means of fluoride	(*131*)
	Chromatography	(*5, 51, 56*)
Co	Complexation by means of fluoride	(*131*)
	Chromatography	(*5, 56*)
Mo	Extraction of Mo chlorides with Et_2O	(*390*)
	Complexation with tartrate	(*161*)
Cu	Extraction of dithizonate	(*240*)
	Extraction of cupferrate with $CHCl_3$	(*58*)
	Chromatography	(*5, 56, 202, 270*)
Hg	Extraction using di-2-naphthylthiocarbazone	(*182*)
	Chromatography	(*56*)
Zn	Extraction of dithizonate	(*18, 58*)
	Complexation with tartrate	(*161*)
V	Extraction of dithiocarbamate complex	(*65*)
Al	Extraction of dithiocarbamate complex	(*65*)
	Complexation with tartrate	(*161*)
	Chromatography	(*197, 261*)
Be	Chromatography	(*261*)
Sulfate	Chromatography	(*75*)
Cyanides	Demasking of cyanide complexes	(*52*)
F	Demasking of fluorides	(*72, 98*)
	Chromatography	(*75, 159*)
Y and Dy	Ion exchange with citrate elution (separation)	(*332*)
Th	Extraction of Th salicylate with EtOAc + Et_2O	(*289*)
Rare earths	Extraction of 5,7-dichloro-8-hydroxyquinolinates	(*230*)
	Volatilization in stream of S_2Cl_2	(*289*)
	Chromatography	(*165*)
Sc	Extraction of quinalizarin complex with AcOEt	(*26*)
Pa	Complexation through use of tartrate	(*137*)
Pd	Extraction of dimethylglyoxime complex into $CHCl_3$	(*389*)
	Complexation as pyrophosphate	(*370*)
Pt	Extraction of Pt(II) dithizonate	(*389*)
Au	Extraction of dithizonate	(*389*)
	Extraction of $HAuCl_4$ using AcOEt	(*370*)

The high-frequency oscillator for titrimetry (*251*) is of potential value for microchemical work, as is the microconductometric titrator suggested by Stock (*335*).

A gas analysis microapparatus employing solid absorbents has been described (*79*) and the iodine meter of Ehmert (*87*) is a significant development. The meter operates on depolarization effects and is sensitive to 10^{-9} microgram of iodine in 1 ml. of solution.

SEPARATIONS

The discussion of separations deals mainly with techniques such as chromatography, extraction, and complexation (see Table I). Precipitation methods are so well established that it seems impractical to attempt their inclusion here. Separation by precipitation is undergoing important development, however, and new organic precipitants, gathering agents, complex reagents, and homogeneous precipitation methods should be considered carefully for the solution of separation problems.

The general review of separation methods by Mellon (*222*) is of importance to the microchemist. The discussion by West (*377*) of the various techniques used in complex separations in metallurgical analysis should also be consulted. The article by Willard and Sheldon (*382*) is thought-provoking as are the papers by Jewsbury and Osborn (*171*) and Murthy and Rao (*245*) dealing with basic salt precipitations. The microscheme of nonhydrogen sulfide of Querol and Wilson (*288*) should find use. Romano has presented a scheme of group precipitations followed by final chromatographic separations (*298*) for use in toxicology. Separations based on density differences as described by Novikov (*254*) have possibilities for microchemical work.

Extraction methods are gaining in popularity. They are often as complete and sharp as precipitation procedures and are usually more rapid to perform. Morrison has reviewed the analytical uses (*233*) of liquid-liquid extraction and Abrahamczik (*1*) has discussed the use of chelating agents in the separation of metals by means of solvent extraction. Gorbach and Pohl (*130*) have suggested various extractions for use in the enrichment of small quantities of metals.

An impressive number of contributions have appeared dealing with the chromatographic (and ion exchange) separation of inorganic materials and the reviews on the subject should be consulted (*193, 263, 274, 312, 348, 355*). Discussions of inorganic capillary analysis (*110*), the comparative value of various organic solvents in paper chromatography (*209*), the effect of humidity and light on the efficiency of certain separations (*208*), the possible use of chelating exchange beds (*223*), and the studies on the nature of inorganic-alumina chromatograms (*313*) are all of fundamental interest.

Lederer (*202*) has reported R_f values for 42 inorganic cations in three different solvents using paper chromatography. Burstall and associates have conducted broad studies on the use of cellulose for inorganic separations (*55, 56*). Pollard and coworkers (*276, 277*) and Lacourt *et al.* (*206*) have likewise made detailed studies of paper chromatography. The use of 8-quinolinol columns has been studied by Robinson (*295*).

The work of Rogers on the separation of minute quantities of metals (*297*) by means of electrodeposition is of special interest.

Table II. Gravimetric Analyses

Subject	Method	Reference
Alkali metals		
Na	Manganese uranyl acetate	(*31*)
Cd	Diantipyrylmethane (pptn. of $CdBr_4^{--}$)	(*393*)
	Salicylaldehyde semicarbazone	(*163*)
Co	Benzhydroxamic acid	(*246*)
Cu	Benzhydroxamic acid	(*246*)
Pb	Chromate	(*224, 225*)
Ge	Various methods	(*152*)
Ni	1,2-Cycloheptanedione dioxime	(*102*)
	Dimethylglyoxime (aqueous soln.)	(*306*)
	Benzhydroxamic acid	(*246*)
Tl	Pptn. as $Co(NH_3)_6TlCl_6$	(*237, 238*)
U	8-Quinolinol	(*265*)
V	Various methods	(*231*)
Zr	Mandelic acid	(*118*)
	Phthalic acid	(*286*)

Table III. Titrimetric Analyses

Subject	Method	Reference
Alkali metals		
Na	Zinc uranyl acetate (alkalimetric titration)	(*30*)
K	Cobaltinitrite (iodometric)	(*80*)
Alkaline earth metals Ca	Ethylenediaminetetraacetate	(*195, 220, 334*)
Halides		
F	$Th(NO_3)_4$	(*330, 331*)
Cl	$FeSO_4.(NH_4)_2SO_4$ titration of free chlorine	(*217*)
	Iodometric (ultramicrodetermination)	(*360*)
	$Hg(NO_3)_2$ (high frequency titration)	(*38*)
S	$BaCl_2$ (sodium rhodizonate indicator)	(*364*)
	$BaCl_2$ (ethylenediaminetetraacetate)	(*236*)
Be	NaOH (high frequency titration)	(*7*)
B	NaOH (mannitol procedure)	(*2*)
Cd	Na_2S (potentiometric)	(*330*)
	Diethyldithiocarbamate	(*314*)
In	Excess Ce(IV) added, back-titrated with $FeSO_4$	(*211*)
Fe	$HgNO_3$(NH4NCS indicator)	(*107*)
	Titration with Ti(IV)	(*109*)
	$KMnO_4$ titration of oxalate	(*90*)
Mg	Ethylenediaminetetraacetate	(*145, 334, 384*)
Mn	Acetylacetone (iodometric)	(*115*)
Hg	Dithizone	(*227*)
Pb	Diethyldithiocarbamate	(*314*)
Ag	NH_4NCS	(*347*)
	Diethyldithiocarbamate	(*314*)
Ti	$Fe_2(SO_4)_3$	(*37*)
V	$FeSO_4$-$(NH_4)_2S_2O_8$	(*113*)
Zn	Diethyldithiocarbamate	(*314*)

GRAVIMETRIC ANALYSIS

The work on gravimetric methods of microanalysis is summarized in Table II. In addition, the methods of automatic gravimetry hold potential promise and thermolysis curves themselves give valuable information to the microanalyst (*82*).

TITRIMETRIC ANALYSIS

One of the most significant trends in titrimetric analysis is the interest in electrometric methods for the detection of end points (*39–41, 76, 208, 251*). High frequency, coulometric, and amperometric titrations are potentially more sensitive than conventional methods based on optical indication of end points and can be expected to undergo careful investigation in the future. The articles describing titrimetric procedures are listed in Table III.

SPOT TESTS

A summary of the development, present status, and prospects for future development of spot tests was presented by Feigl and West (*101*). Hahn (*146*), Gillis (*120, 121*), and Malissa (*216*) have discussed the question of detection limits and methods for expressing sensitivities. West and Hamilton have studied the variation in sensitivity (*376*) of selected tests caused by variation in reaction media (as much as a hundredfold change in sensitivity may be found in going from one spot-test paper to another).

Reports on the application of spot tests include studies of cellulosic fibers (*219*), metal finishes (*206*), nickel alloys and stainless steels (*200*), bauxite (*97*), steels (*294*), toxicology (*298*), and industrial wastes (*58*).

Odekerken has published (*255*) a spot-test scheme for identification of a large number of anions. Přibil (*280, 281*) and Tsubaki (*353*) have suggested tests for various ions. Individual spot tests are listed in Table IV.

COLORIMETRIC ANALYSIS

Table V listing various colorimetric determinations is presented as correlative material because of the close relationship between colorimetry and microanalysis. Critical discussion of the principles and methods of colorimetry will be found under the review of absorption spectrophotometry.

In addition to the determinations listed in Table V, a number of colorimetric procedures are collected and presented in the papers by Barnard and Telford (*20*), Butts and collaborators (*59*), Murakami (*243*), Rasmussen and Rodden (*293*), and Jones (*176*).

Table IV. Spot Tests

Subject	Reagent or Method	Reference
Alkali metals		
Na	Fluoaluminic acid	(*23*)
	Fluoferric acid	(*23*)
	Resorcinolsulfonic acid	(*24*)
Li	6,8-Dichlorobenzoyleneurea	(*25*)
	1,8-Dihydroxyanthraquinone	(*307*)
Rare earths		
Ce	Benzidine	(*244*)
Platinum metals		
Pd, Pt, Rh	*p*-Nitrosodiphenylamine	(*302*)
Halides		
Cl	Fluorescein + KBr	(*144*)
Br	Fluorescein	(*144*)
F	Etch test	(*383*)
	$Al(OH)_3$ + indicator paper	(*71*)
Sulfur family		
Sulfide, sulfite	MnO_2 and benzidine and thiosulfate	(*162*)
Thiocyanate	Catalysis of iodide-azide reaction	(*317*)
Al	1,8-Dihydroxyanthraquinone	(*307*)
Sb	Gossypol	(*371*)
	$Na_2S_2O_3$	(*252*)
	$H_3PO_4.12MoO_3$	(*339*)
Bi	Cinchonine + KI	(*339*)
	6-*tert*-Butyl-3-methylphenol	(*234*)
Cd	Diantipyrylmethane + NCS^-	(*393*)
Co	Diantipyrylmethane + NCS^-	(*393*)
	Antipyrine	(*257*)
	Dimethylglyoxime	(*209*)
	Alkali hydroxides [to form $Co(OH)_4$-$(H_2O_2)_2^{--}$]	(*132*)
Cu	*o*-Nitrosophenol	(*278*)
	Antipyrine	(*257*)
	Catalysis of KH phthalate decomposition	(*45*)
	Aniline	(*287*)
	Various tests	(*258*)
Au	Pararosaniline hydrochloride	(*370*)
	Catalytic	(*147*)
Hf	Various tests	(*256*)
Fe	2-Thenoyltrifluoroacetone	(*62*)
	Catalysis of KH phthalate decomposition	(*45*)
	Citrinin	(*207*)
	Thioglycollic acid	(*34*)
Mg	Eriochrome gray SGL and BL	(*184*)
	1,8-Dihydroxyanthraquinone	
Mn	Diacetyloxime thiosemicarbazone	(*164*)
	p,p'-Tetramethyldiaminodiphenylmethane	(*285*)
Ni	Dimethylglyoxime	(*66*)
Si	Molybdate + benzidine	(*72*)
Ag	Various tests	(*248*)
U	Oxalohydroxamic acid	(*73*)
	Fluorescence in ultraviolet light	(*212*)
V	Various tests	(*373*)
Zn	$K_4Fe(CN)_6$	(*252*)
	Dithizone	(*78*)
H_2O_2	PbS (observe fading under ultraviolet light)	(*114*)
	MnO_2 and benzidine	(*163*)
Cyanide	Turnbull's blue	(*154*)
Carbon monoxide	$(NH_4)MoO_4$ + $PdSO_4$	(*321*)

ORGANIC REAGENTS

The development of organic reagents and the design of new reactions for their use are probably the most important field in the general development of inorganic microchemistry. Consideration of the literature of microchemical methods shows the use of organic reagents in separations as sequestrants, precipitants, ion exchange materials, elutants, and extractants. Certainly, the progress in gravimetry, titrimetry, colorimetry, and spot tests is controlled significantly by the availability of new reagents.

Some articles have appeared which have general interest, including the paper on ion exchange beds having free chelating groups (*223*) and the discussion by Feigl and Schaeffer (*99*) of the destruction of chelates by wet oxidation so that masking effects can be eliminated. West and Conrad (*372*) made a study of coprecipitation occurring in the use of some organic precipitants, and Blay and Warren (*42*) have pointed out that pure 1-nitro-2-naphthol is not a reagent for cobalt, as reported, but is contamination of the parent nitroso compound that gives rise to reactivity.

The reactivity of certain functional groups and the development of some organic reagents have been reviewed by Jonckers (*174*). The reactions of metals in molten 8-quinolinol (*96*) has interesting implications.

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Table V. Colorimetric Analyses

Subject	Method	Reference
Alkali metals		
K	Cobaltinitrite + Griess reaction	(*378*)
	Dipicrylamine	(*320*)
Alkaline earth metals		
Ca	Pyrogallolcarboxylic acid	(*259*)
	NH_4 purpurate	(*262, 269*)
	Chloranilic acid	(*205*)
Rare earth metals		
Ce	Benzidine	(*244*)
Platinum metals		
Os	Thiourea	(*83*)
Pd	1-Nitroso-2-naphthol	(*6*)
Pt	$SnCl_2$	(*10*)
Ir	$HClO_4$ + H_3PO_4 + HNO_3	(*11*)
Ru	Dithio-oxamide	(*14*)
	Thiourea	(*13*)
Halides		
OCl^-	Phenol + aq. NH_3	(*363*)
Cl_2	*o*-Tolidine	(*343*)
F	Zr alizarine lake	(*44*)
	Silicomolybdic acid	(*35*)
	Ti + H_2O_2	(*189*)
Cl	$AgNO_3$ + ultraviolet light	(*340*)
	$AgNO_3$ followed by dithizone titration	(*168*)
Sulfur family		
SO_4^{--}	Zn acetate (pptn. of ZnS)	(*299*)
NCS^-	$Fe(NO_3)_3$	(*127*)
Al	Stilbazo	(*195*)
Sb	Alizarine S	(*16*)
	$H_2PO_4.12MoO_3$	(*339*)
As	Gutzeit method	(*169, 228*)
	Molybdic acid	(*104*)
Be	Aurintricarboxylic acid	(*190*)
	Sulfosalicylic acid	(*221*)
Bi	Thiourea	(*57*)
	Various methods	(*210*)
	Cinchonine	(*339*)
B	Morin	(*170*)
	Chromotrop 2B	(*153*)
Cr	Diphenylcarbazide	(*242*)
Co	Thiocyanate + ethyl alcohol	(*356, 376*)
	Dimethylglyoxime	(*279*)
	HCl	(*392*)
	o-Nitrosocresol	(*28*)
	Tetraphenylarsonium chloride	(*17*)
Cu	Sodium diethyldithiocarbamate	(*28, 239, 315, 366*)
	Direct green B	(*272*)
Cu (*Contd.*)	HBr	(*322*)
	Dithizone	(*240*)
	Dithio-oxamide	(*226, 386*)
	Pyridine + salicylic acid	(*131*)
	Cuproin	(*161*)
Au	*o*-Tolidine	(*309*)
Fe	Thiocyanate	(*15, 68, 304*)
	Thioglycolic acid	(*17, 322*)
	1,10-Phenanthroline	(*17, 138*)
	2,2′-Bipyridine	(*17, 138*)
	Ferron	(*149*)
	Dimethylglyoxime	(*150*)
	Pyrocatechol	(*151*)
	Citrinin	(*207*)
Mg	Titan yellow	(*70, 260*)
	8-Quinolinol + sulfanilic acid	(*271*)
	p-Nitrobenzene-azo-1-naphthol	(*95*)
Mn	Ethylenediaminetetraacetate (+ bismuthate)	(*282*)
	Tetramethyldiaminodiphenylmethane	(*69, 285*)
	Periodate	(*94*)
Hg	Dithizone	(*359*)
	Di-2-naphthylthiocarbazone	(*182*)
Mo	Pyrocatechol	(*316*)
	H_2O_2	(*344*)
	Thiocyanate	(*135*)
	Phenylhydrazine hydrochloride	(*12*)
Ni	Dimethylglyoxime + strong oxidant	(*17*)
	Dimethylglyoxime	(*63, 66, 126*)
NO_3^-	Phenoldisulfonic acid	(*172, 342*)
	Hydrostrychnine	(*139*)
	2,4-Xylenol	(*21*)
Sc	Quinalizarin	(*26*)
Si	Molybdate (extraction with BuOH)	(*104*)
	Molybdate	(*140*)
Ag	Rhodanines	(*4*)
Tl	Benzidine	(*192*)
W	$SnCl_2$	(*113*)
U	Various reagents	(*365*)
	H_2O_2	(*362*)
	Oxalohydroxamic acid	(*73*)
V	Dithiocarbamate	(*65*)
Zn	Dithizone	(*105, 275*)
Zr	Alizarine S	(*141*)

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FLUOROMETRIC ANALYSIS

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THIS review on fluorometric analysis covers the 2-year period from approximately October 1949 to October 1951, and is a continuation of previous surveys (*170*, *171*).

BOOKS AND GENERAL ARTICLES

Several books have been published during this period which are of interest from a general standpoint. Under the title, "Lumineszenz," Bandow (*7*) has compiled a book on the applications of fluorescence in physics, chemistry, and biology. The chief value of this book to the analyst is in the review of German literature. Strugger's (*155*) treatise on the use of fluorescence microscopy in microbiology gives the general techniques, names many of the fluorescent dyes used, shows the effect of pH, and lists 102 references. Leverenz (*98*) gives an excellent treatment of the theory of fluorescence and phosphorescence of solids, scintillation counters, and the composition of phosphors; 750 references are included. Kroger's (*93*) book, which is also concerned with the fluorescence of solids, includes tables giving the fluorescence of many inorganic compounds. Curie (*27*) in a book on the general topic of fluorescence and phosphorescence discusses the general theory of the production of luminescence in organic and metallo-organic complexes and the relation of fluorescence to the constitution of the molecule. A chapter on cathode luminescence, triboluminescence, chemiluminescence, etc., is also included. Foster (*52*) has published a book on fluorescence of organic compounds which does not give analytical applications, but is of interest from a theoretical standpoint. Sandell (*138*) in the second edition of his text gives fluorometric methods for aluminum, beryllium, gallium, indium, scandium, thallium, uranium, zinc, and rare earths. He also includes a theoretical discussion on the application of the Beer-Lambert law to fluorescence in the same vein as the excellent development of this topic by Lothian (*101*) and Kavanagh (*84*).

Several general articles on fluorometric analysis have appeared. Déribéré (*34*) reviews recent applications of ultraviolet light in analysis; Radley (*131*) discusses fluorescence methods in the food industry; White (*172*) gives specific procedures and apparatus for use in the usual scheme of qualitative analysis; and Levskin (*100*) reviews the advances in luminescence analysis with 51 references.

APPARATUS

Sources of Ultraviolet Radiation. A new series of lamps for both the longer ultraviolet light at 3650 A. and the shorter at 2537 A. has been announced by Ultra-Violet Products, Inc. (*162*). These lamps are of convenient laboratory type and are equipped with mercury vapor lamps and 360 B. L. tubes. Several firms (*154*, *162*) now market fixtures for 4-watt fluorescent lamps which may be used with the 360 B. L. tubes for qualitative analysis. As these fixtures are made for daylight lamps, the reflectors are usually white enamel and should be replaced by aluminum reflectors for ultraviolet lamps.

The Menlo Research Laboratory (*108*) sells an instrument known as a daylight fluorescence tester which includes a viewing apparatus and a source of ultraviolet radiation activated by a battery or ordinary power supply. An interchangeable head converts the source to either 3650 or 2537 A.

Fluorometers. A new fluorometer has been widely advertised by the Central Scientific Co. (*24*). This instrument is equipped with two phototubes, so that measurement may be made on

fluorescent solutions over the entire visible spectrum. Several instrument makers (*3, 128, 161*) have developed moderately priced line-operated electron multiplier photometers which are equipped with a unit that is easily adapted to the measurement of fluorescent light.

Directions for making and improving fluorometers have been given by many authors along with discussions of particular methods. Alford and Daniel (*1*) have devised an especially stable, sensitive, and flexible instrument using a VX-41A electrometer tube as an amplifier in a DuBridge-Brown type circuit. Kaufman (*83*) and his associates have improved the Argonne Model XI fluorometer and use an AH6 lamp to increase sensitivity. Fletcher and May (*49*) have built a transmission fluorometer for use in the determination of uranium in fluoride melts. In this instrument, the sample is placed between the ultraviolet source and the photocell. This makes a simple arrangement of the optical parts and is about ten times as sensitive as a reflection-type instrument with the same amplifying unit.

Hilger and Watt in England have designed an instrument for the measurement of the fluorescence of solids, in which the optical parts are all on a horizontal axis. In this apparatus the ultraviolet rays from a mercury vapor lamp pass through a condenser and are reflected by a mirror to the sample. Another mirror picks up the fluorescent light and transmits it through a lens system to a photoelectric multiplier tube. Davey and Florida (*29*) have given this fluorometer extensive tests and conclude that the workmanship is excellent. They suggest that the turntable holding the sample be changed to a slide in order to facilitate the operation of this unit. Wheelock (*169*) describes a fluorometer designed with a water cooling jacket around the mercury vapor lamp. Wokes and Slaughter (*179*) have increased the sensitivity of the Spekker instrument 75-fold by replacing the barrier layer cells with a photomultiplier tube. The general use of electron multiplier phototubes in the measurement of weak light intensities is discussed by Oldenberg and Broida (*121*) and a balanced circuit type of instrument is described. Stephen (*153*) uses an instrument for the determination of thiamine by which 750 galvanometer units are registered with 1 microgram of thiamine in 10 ml. of solution.

A comparison fluorometer of high sensitivity is described by Larsen (*95*), in which an automatic device switches the light from the known to the unknown sample at 60 cycles per second. Minard and Eicher (*110*) have devised a two-channel fluorometer for in vivo studies to measure the time of appearance and rate of change of fluorescein on tissue areas after injection. At the Pittsburgh spectroscopy conference, Priestley (*129*) described a modification of the Beckman spectrophotometer in which he used a 1P28 electron multiplier tube with a Brown recorder to determine the fluorescent spectra of polycyclic hydrocarbons.

An apparatus to facilitate the excitation and observation of chromatographic columns, developed by an instrument company (*127*), consists chiefly of an arrangement whereby a mercury vapor lamp is easily passed over the column. Brumberg (*21*) has devised an apparatus which he calls an ultrachemiscope for examining paper chromatograms. In this instrument the ultraviolet light passes through the paper and strikes a fluorescent screen. This screen is made of materials that are excited by different wave lengths of energy and produce different colors; hence the absorption pattern of the paper is easily observed. Brockman and Beyer (*19*) use photographic techniques for recording the fluorescent zones on chromatographic columns. Harvalik (*72*) has employed an electronic image converter for studying the fluorescence in chromatography when the exciting rays extend from the ultraviolet to the infrared.

Recording spectroradiometers have been developed by Parsons and his associates (*123*) for the automatic recording of the energy distributions emitted by luminescent materials. The fluorescent spectra of dyestuffs on cloth have been obtained with modifications of the Carey (*109*) and Beckman (*143*) spectrophotometers.

Vendt (*164*) claims that an excellent condenser and filter for the excitation rays in the 3650 A. range can be made by filling a 40- or 60-watt clear electric light bulb with 10% cobalt sulfate solution. The use of a solution of tetrammine cupric sulfate as a filter in fluorescence microscopy is described by Zanikov (*181*).

Quinine sulfate has long been used as a standard in setting instruments. Bird (*12*) finds that this compound is adsorbed on the walls of test tubes after long standing. Treatment of the tubes with hot alkali renders them nonadsorptive.

INORGANIC APPLICATIONS

Aluminum. For some years the fluorescence of the 8-quinolinol complexes of gallium and indium dissolved in chloroform has been used in the determination of these elements. It has now been shown that this same method may be employed for the analyses of aluminum. Tullo (*160*) and his associates have applied this method for the determination of aluminum in beer; and Grimaldi and Levine (*64*) use it for the analysis of aluminum in phosphate rock. In both cases the method is rapid and accurate for even extremely small quantities. In rock analysis a great advantage lies in the fact that small original samples can be used. Wiberley and Bassett (*174*) describe the procedure where aluminum oxinate is dissolved in chloroform as a colorimetric method for determining aluminum in steel; in another article (*9*) they indicate that the fluorescence of the chloroform extract may also be used as a measure of the aluminum concentration.

Kulberg and Mustafin (*94*) report that certain of the chlorohydroxyanthraquinones form fluorescent complexes with aluminum which are not destroyed by concentrated hydrochloric acid. If this fluorescence is sufficiently intense for analytical purposes, the reaction may be very useful, as the other fluorometric reagents are ineffective in even dilute hydrochloric acid.

Rouir and Deitz (*136*) have found the morin method useful for determining quantities of aluminum in the range of 0.001% in bronzes and brasses. Bishop (*16*) has made an extensive study of the effect of anions on the morin test for aluminum, gallium, beryllium, and zinc, and has shown that the aluminum-morin complex may be used as a sensitive test for citrate, fluoride, oxalate, phosphate, tartrate, and vanadate ions. A 0.2% solution of morin in 0.01 *N* sodium hydroxide is recommended for qualitative work; the alcohol solution is more sensitive and should be used when quantitative results are desired. Morin is used by Klemperer and Martin (*90*) as the reagent for the determination of beryllium in biological materials. The smallest amount detected by this method was 0.05 microgram.

The applications of 8-quinolinol (oxine, 8-hydroxyquinoline) as a reagent in fluorometric analyses are numerous. Gentry and Sherrington (*58*) have determined the pH conditions for the complete extraction with chloroform of the oxinates of molybdenum, iron, tin, copper, nickel, aluminum, and manganese. They show that this is a useful method for the separation of these metals and state that the chloroform solution may be used for the fluorometric determination as well as for the direct colorimetric analyses. Feigl and Heisig (*46*) have studied the detection of calcium, magnesium, and aluminum on paper with 8-quinolinol as the reagent. Aluminum is the only one of these in which the fluorescence will persist in the presence of acetic acid vapor. If the paper is exposed to fluoride vapor, the aluminum 8-quinolinol diminishes in fluorescence and a test for fluoride results. A test for cyanide ion is based on the liberation of 8-quinolinol from the copper complex and the determination of the 8-quinolinol with aluminum.

Beryllium may be separated from aluminum qualitatively with paper chromatography and both identified by spraying with 8-quinolinol (*122*). The beryllium moves considerably faster than aluminum if a solvent of 80% butanol and 20% concentrated hydrochloric acid is used. An extensive study of the analytical applications of the 8-quinolinol derivatives of gallium and thallium has been made by Moeller and Cohen (*112*) and their article

should be read by anyone using the chloroform extraction of oxinates. Dudley (*36*) has shown that the gallium oxinate–chloroform method may be used in the determination of gallium in animal tissue.

White and associates (*173*) have used the lithium–8-quinolinol complex for the determination of lithium in rocks. This serves as one of the simplest methods of comparing the lithium content of reagents to a standard.

The fluorometric method for the determination of uranium, which uses the sodium fluoride melt, has been reviewed in several publications (*44, 53, 116, 130, 134*). Grimaldi and his associates (*65*) have applied this method to the determination of uranium in shale and phosphate rock for field as well as laboratory use.

Willard and Horton (*175*) have studied a number of the colorimetric and fluorometric indicators for the titration of thorium with fluoride. Of the 200 compounds used 162 showed no change in either the visible or ultraviolet light, and among these morin and quercetin were the best fluorescence indicators. With these latter indicators, the results of the fluoride titration (*176*) were better than those with alizarin red S when the fluoride was in amounts greater than 2 mg.

Alford and others (*2*) have introduced flavonol as a new fluorometric reagent for zirconium. The fluorescence of this complex is very intense and it persists in 0.2 *N* sulfuric acid solution. Hafnium is the only other element that gives a fluorescence with flavonol in 0.2 *N* sulfuric acid. The method greatly simplifies the determination of zirconium in ores.

In a paper concerned with the colorimetric determination of boron with 1,1-dianthrimide, Ellis and his associates (*40*) show that 1-amino-4-hydroxyanthraquinone may be used for the quantitative determination of this element by measuring the fluorescence in concentrated sulfuric acid solution. They prefer the 1,1-dianthrimide reagent. In an article on the use of ultraviolet light in the food industry, Radley (*131*) suggests that fluorometric methods be used for boron, sulfur dioxide, and reducing agents.

A rather unusual use of fluorescence in analysis has been described by Brumberg and others (*22*), who utilize the absorption characteristics of various compounds to indicate the end point in titrations. Filtered ultraviolet light is passed through the solution being titrated and permitted to come in contact with a fluorescent screen. The end point is observed by the appearance or extinction of the fluorescence.

A qualitative test for zinc and cadmium is indicated by Denigès (*33*) as a result of a study of the reaction of resorcinol with phthalic anhydride. Resorcinol in concentrated hydrochloric acid with zinc gives a green fluorescence and with cadmium produces a violet-rose colored solution which does not fluoresce.

The application of fluorescence microscopy in mineralogy has been reviewed by Haberlandt (*71*) and 79 references are given. This same author has determined the fluorescent spectra of several minerals (*70*) and has made an extensive study of the rare earths in fluorite (*69*). The fluorescent test for some of the rare earths can be extremely sensitive—for example, 0.001 microgram of yttrium can be easily detected (*119*). Niobium and uranium (*106*) in columbite can be detected through the sodium fluoride fusion technique. Wilson (*177*) has studied the fluorescence of feldspars with short-wave-length ultraviolet light and indicates that this is a useful property for distinguishing feldspar from other minerals. Dement (*32*) and Hershey (*74*) have published tables showing the fluorescence of many minerals.

It is a question whether the x-ray fluorescence method of analysis belongs in this review or under spectrographic methods. In this technique the exciting ray and the emitted rays are both in the x-ray region and the emission is detected with a Geiger tube. Solid specimens are used for analysis and are not altered or destroyed. Birks and his associates have applied this method to the determination of lead and bromine in ethyl fluid (*15*) and to the analysis of mixtures of hafnium, zirconium, columbium, tantalum (*13*), and uranium (*14*).

ORGANIC APPLICATIONS

Acetol may be determined fluorometrically by reaction with *o*-aminobenzaldehyde to form 3-hydroxyquinaldine (*51*). This is sensitive to 0.3 mg. of acetol per liter.

Thornton and Speck (*158*) have devised a procedure for the determination of pyruvaldehyde which is based on its reaction with chromotropic acid. The product has an intense green fluorescence which gives a straight-line relationship for concentrations of pyruvaldehyde from 0.0 to 1.5 mg. per liter. A method designed for the analysis of 2-nitronaphthalene in the presence of 1-nitronaphthalene depends on the sulfonation and reduction of these compounds. Filters are used to exclude the dull green fluorescence of the alpha isomer and the intensity of the blue fluorescence of the beta isomer is measured. The procedure detects 0.05% of the beta isomer (*43*).

Benzil may be determined by its condensation product with *m*-diethylaminophenol (*141*). This reaction forms a blue-red dye with a yellow-red fluorescence. Benzil concentration up to 0.03 mg. per ml. gives a straight line when plotted against galvanometer readings. Alkylated aminophenols can be determined by the condensation reaction with diketones.

A qualitative fluorescence test for malic acid has now been applied quantitatively by Leininger and Katz (*97*). This involves the reaction of malic acid with 2-naphthol in the presence of concentrated sulfuric acid to produce a very highly fluorescent benzocoumarin. Hummel (*78*) uses orcinol as the reagent for the determination of malic acid. The methyl coumarin produced has a bright blue fluorescence.

Alloxan monohydrate may be determined as riboflavin when condensed with D-1-ribitylamino-2-amino-4,5-dimethylbenzene hydrochloride (*159*).

A qualitative test for acenaphthene is achieved by nitrating this compound and then boiling it with lead in the presence of glacial acetic acid (*180*). This reaction produces a compound which has a green fluorescence and is specific for acenaphthene. Radley (*131*) uses acenaphthene 5-carbolic acid to test for formaldehyde; these two compounds react in sulfuric acid to produce a greenish yellow fluorescence. Under the same conditions tartaric acid produces a yellow blue, glycerol a yellow, and ethylene glycol a golden yellow fluorescence. Anthrone (*132*) also serves as a reagent for the latter three substances.

The variation of the intensity of fluorescence with pH gives a characteristic curve, which in some cases can be used for identification purposes. Curves of this type have been found to be similar for flavin compounds and these curves differed from those of the 4-pteridine series (*85*). The color and relative intensity of fluorescence of 98 coumarin derivatives over a pH range of 1.6 to 12.6 have been reported (*61*). The influence of the position of the hydroxyl, carboxyl, and methyl groups is definite. The use of these pH curves in identification of compounds is shown by data on scopoletin, which gives a pH–fluorescence intensity curve similar to the coumarin from avena roots. Sixteen synthetic coumarins were tested for change in fluorescence over the range of pH 3 to 10, and seven showed marked color change near the neutral point (*118, 148*).

The presence of chlorophyll in living chloroplasts may be observed by fluorescence microscopy. When the temperature on the cell structure is suddenly increased, the red fluorescence of the entire chloroplast shows a great increase in intensity (*59*). This increase in fluorescence, observed under the microscope, presents a simple means of making a submicroscopic alteration evident which may not be seen by the ordinary microscope.

Phthalic acid esters may be determined by treating them with sulfuric acid to form phthalic anhydride, which is in turn fused with resorcinol to produce fluorescein (*163*). Gage and Wender (*56*) have shown that binary mixtures of flavonol-3-glycosides can be separated by paper partition chromatography and the individual pigment zones located with ultraviolet light.

The fluorescences of acridine and many of its derivatives have

been measured by Villemey (*165*). For low concentrations the intensity of the fluorescence was found to be proportional to the concentration. The fluorescent spectra of the acridine derivatives were also determined. The fluorescence spectra of several polycyclic aromatic compounds have been determined by Scott (*145, 147*). The usual correlation between the corresponding absorption and fluorescence spectra was found and the effect of the substituent groups was determined. The use of fluorescence as an analytical tool does not seem promising for the study of high polymers (*157*).

Conrad (*26*) has shown that the aromatic hydrocarbons in gasoline can be identified by a combination of chromatographic and absorption techniques. Parasheen, a highly fluorescent substance soluble in hydrocarbons, is added before adsorption of mixture on a silica column. Fluorescent methods are reported to hold promise for geophysical prospecting and soil analysis for petroleum (*45, 151*). The chromatographic fraction of black oils is described by Lawrence and Barby (*96*) and the dispersion, color, and fluorescence data for various fractions are recorded. Carcinogenic substances, chiefly 3,4-benzopyrene, in tars and resins have been determined by the fluorescence of the paraffin oil extract of these substances (*79*). By this method 5×10^{-6} gram of 3,4-benzopyrene per gram of tar is easily detected. Fluorescence offers a means of distinguishing trans-trans from cis-trans configurations in the 1,4-diarylbutyldienes (*75*).

BIOLOGICAL APPLICATIONS

In a review of the use of ultraviolet radiation in the food industry, Radley (*131*) discusses the examination of oils, fats, milk, etc., and describes the tests for organic acids, sugars, glycerol, and preservatives. Bergholts (*11*) has assembled a review with 90 references on the use of luminescence analysis of some biologically active substances in animal organisms.

The determination of vitamins B_1 and B_2 continues to be the subject of considerable research. Gstirner (*68*) in Germany and the Association of Vitamin Chemists (*5*) in this country have published books which include the recommended methods for vitamin assay. A report from the Subcommittee on Vitamin Estimations of the British Society of Public Analysts gives an excellent review of the fluorometric method for B_1 (*30*). Ridyard (*133*) has made an analysis of the factors affecting the recovery of B_1 and presents a theoretical discussion of the fluorometric estimation from the standpoint of Beer's law. Stack (*152*) recommends that a solution of 0.0001 gram of quinine per 100 ml. of 0.1 *N* sulfuric acid be used as a standard for thiamine determinations. Thiamine determination in wheat flour and bread is given by Petit (*126*). The determination of thamine in urine has been dealt with by several authors (*115, 120*). Methods of removing impurities have been devised and perfect recovery of added thiamine is claimed.

Collaborative results of the Association of Official Agricultural Chemists (*102*) indicate that the fluorometric method for vitamin B_2 compares favorably with the microbiological method. This report shows that there is no statistically significant difference between the two. Klatzkin and his associates (*89*) in working with malted preparations have obtained much better agreement with the fluorometric method than with the microbiological in the determination of riboflavin. Hoshino (*77*) and his associates give data for riboflavin determination in 40 foods and Engel and Hendricks (*41*) have determined it in cattle foods. The lumiflavin method for the determination of vitamin B_2 has been used on various natural products (*55, 81, 82, 92, 107, 135, 166*). In general, the lumiflavin which is formed by irradiation of riboflavin is extracted with chloroform and determined by the intensity of its fluorescence rather than by extinction or colorimetric methods. The chemical determination of vitamin B_{12} by colorimetric and fluorometric methods is described by Boxer and Richards (*18*). The latter method employs the reaction with alloxan, forming highly fluorescent 6,7-dimethylalloxazine.

The composition of the fluorescent oxidation product of adrenaline has been postulated by Lund (*104*) and Ehrlén (*38*). Lund has studied the determination of adrenaline extensively (*103, 105*). In the fluorometric procedure adrenaline is oxidized with manganese dioxide to adrenochrome, which is converted by alkali to the highly fluorescent adrenolutine. Ascorbic acid will prevent the oxidation of adrenolutine by the air. By comparison of the fluorescence of sample with and without ascorbic acid present, the adrenolutine content can be determined. Annersten and associates (*4*), and others (*66*) report excellent results for the determination of adrenaline, in which sodium thiosulfate is used to prevent oxidation and, for comparison, the fluorescence of adrenaline is extinguished with formaldehyde. The concentration of the alkali in this determination is important (*48, 73*). Natelson and others (*117*) have shown that adrenaline solution in aqueous ammonia containing a primary amine yields a fluorescent product which can be extracted with butyl alcohol. Paper chromatography has been applied to the determination of adrenaline by Shea (*149*). The chromatograph is developed by holding the paper in ammonia fumes.

The fluorometric method for the determination of natural estrogens in various products has been described by several authors (*39, 42, 67*). The method of Garst and others (*57*) is based on the condensation reaction of phenolic steroids with phthalic anhydride. Fierro del Rio and Arrieta Aupart (*47*) use antimony chloride as a reagent to give a green fluorescence with estrone and estradiol. The fluorescent spectra of nine natural estrogens after heating with sulfuric acid have been determined by Bates and Cohen (*10*). Dhéré and Laszt (*35*) in an article on an absorption and fluorescence study of the Salkowski reaction report data that are of interest in the determination of estrogens.

Aureomycin in buffered solution can be determined by its yellow fluorescence (*99, 139*) and the sensitivity can be increased by extraction with *n*-butyl alcohol (*140*). Saltzman (*137*) claims that the accuracy of the fluorometric method for aureomycin is about the same as that of the microbiological method.

The Banierjees (*8*) have reported on the use of the fluorometric method for estimating nicotinamide in cereals, legumes yeast, vegetables, and animal matter. The procedure avoids interfering vegetable components. Carpenter and Kodieck (*23*) give detailed directions for the determination of N^1-methylnicotinamide in urine and its differentiation from coenzyme 1.

The fluorometric procedure for the determination of tryptophan has been the object of considerable study. This is based on the green fluorescence produced by tryptophan in perchloric acid. Indole is shown not to interfere and a linear relationship is obtained for as low as 1 to 8 micrograms of tryptophan (*62*). Of twenty amino acids examined only tryptophan, histidine, and citrulline exhibited a fluorescence (*178*). The technique for the study of nucleic acids by means of paper chromatography and ultraviolet photography is described. Goeller and Sherry (*60*) and Schou (*146*) have reported that pyridine nucleotides in the blood may be determined by the fluorescent compound which results when these materials are heated with alkali in acetone. Various inorganic ions have been found to have an extinction effect on the fluorescence of xanthopterin (*168*) and a quantitative study of the fluorescence spectra of this compound and folic acid has been made (*31*). The antihistaminics, which are 2-substituted pyridine derivatives, form fluorescent compounds by means of a modified cyanogen bromide reaction which may be useful in their determination (*124*). A method of distinguishing ether-insoluble urinary porphyrins from uroporphyrin is based on the red fluorescence of these compounds in conjunction with adsorption and leaching procedures (*20*).

The fluorometric determination of rotenone has been studied by Fonseca (*50*). Rotenone gives a blue fluorescence in alcohol, chloroform, acetone, and benzene, but is green in carbon tetrachloride. The chloroform extract seems best for the analysis. Pesez (*125*) has shown that gitoxin in phosphoric acid gives an intense bluish green fluorescence which may be used to deter-

mine this substance. The fluorescence band of gitoxin under the conditions outlined is from 4600 to 5700 A. Alkaloids of *Rawolfia serpentina* (*6*) and of ergot (*114*) have been determined by fluorescence methods and the calabash curare alkaloids have been identified by their fluorescence after a paper chromatographic separation (*144*). In the microdetermination of belladonna, quinine sulfate serves as an excellent fluorescent acid-base indicator (*91*).

The fluorometric method for the determination of quinine in oily medicines is claimed by Jagle (*80*) to be more rapid, simple, and precise than older methods. Several natural products such as peanut oil and oleic acid have been analyzed. The oil solution in ether is extracted by agitation with 0.1 *N* sulfuric acid. The fluorescence intensity of this sample is read in a fluorometer and then it is treated with concentrated hydrochloric acid and read again; the difference in readings is indicative of the quinine present. The assay of commercial quinine solutions also presents a practical use of fluorometric analysis (*63*). Edgar and Sokolow (*37*) have recorded their experiences with the fluorometric determination of quinidine in blood and reach the conclusion that the method is good for clinical purposes.

The antitrypanosome drug, antrycide, forms a highly fluorescent salt with eosin which permits identification of the drug in concentrations of 40 micrograms per liter of plasma with considerable accuracy. As no other tertiary base reacts with the dye, the method is specific (*150*). The determination of 3-hydroxyanthranilic acid in metabolism studies may be accomplished by fluorometric means (*17*). The enzyme decomposition product of 3-hydroxyanthranolic acid is nonfluorescent.

A new test for identifying bile acids has been devised by Mizuhara (*111*). The bile acid is dissolved in alkaline solution and potassium ferricyanide is added. The solution is extracted with butyl alcohol and the extract is examined under ultraviolet light. The color of the fluorescence is characteristic of the position of the ketonic group.

Qualitative examination of flours such as wheat, corn, and soybean under ultraviolet light is an important aid in classifying flours (*86*). The identification of 2-chloro-4-dimethylamino-6-methylpyrimidine, which is sold as a rat poison, may be accomplished by observing the fluorescence after its reaction with resorcinol (*54*). Christensen and Latif (*25*) have used fluorometric methods successfully in the assay of senna leaves. A special fluoro-illuminator has been designed by Schiller (*142*) for observing cutaneous fluorescence when it is used as an indicator of capillary circulation. Mose and his associates (*113*) have used a water extract of thioflavine S for fluorescence visualization of the blood vessels. This reagent is not toxic; it has a strong affinity for the blood vessel walls, and is strongly fluorescent.

Fluorescent microscopy finds many applications in the identification of certain biological materials. Wagner (*167*) uses thioflavin S as a stain for erythrocytes. Strugger (*156*) discusses the general procedure for staining live cells with fluorescent dyes and gives 40 references. This same topic is the subject of articles by Hofler (*76*) and Dangl (*28*). The possibility of the use of fluorescence in the study of lignin has been investigated by Kisser and Wittmann (*88*). The applications of fluorescence microscopy in food and drug analysis are reviewed by King and Weston (*87*). Their paper includes a diagram of the ultraviolet illumination arrangement and a description of the techniques employed in the examination of solid and liquid materials.

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ELECTROANALYSIS

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THE present article is a continuation of the last review (*2*), and covers the major work of 1949 and 1950 and a large part of 1951, as well as material published earlier but not available until after the last review was written. In comparing the literature reviewed it is interesting to discover that, although the present paper covers a shorter period, there is a very considerable increase in the number of publications in this field. That this is greater than the 17% increase in all technical publication, and is not entirely the result of the declassification of secret wartime documents, can be discovered by qualitatively examining the names of the contributors and the individual papers. The bibliography shows that electroanalysis is increasingly occupying the time and efforts of leaders in analytical chemistry, and has attracted new investigators, who have devoted considerable effort to the preparation of individual series of articles. At the same time, many familiar authors continue actively in this field. This betokens a healthy condition for a well developed area of analytical chemistry which was for a time thought to be "worked out."

BOOKS

No recent books are devoted entirely to electroanalysis, although two or three publications in book form have been published. The most comprehensive and the most notable is a section of a monograph by Böttger (*8*), which is a revision of his earlier publication. It contains an unusually good bibliography and covers, in a critical fashion, the many procedures available in electroanalysis. It is regrettable that 1949, which saw the appearance of this book, also marked the death of Böttger (*20*), a contributor for many years to this branch of chemistry.

The publication of previously classified material from the Manhattan Project has made it possible for Casto (*17*) to report on methods of electrolytic separation using the mercury cell, and separation methods for uranium on solid electrodes. Other important electroanalytical investigations are reported in the same volume. A short review article by Ashley (*4*) attempts in concise form to summarize the present state of development of electroanalysis in its many branches. New work on the separation of inclusions from steels is presented by Klinger and Koch (*51*).

REVIEW ARTICLES

Recent review literature includes a general coverage of electrical methods by Furman (*33*), a review of progress in electroanalysis in Germany during the war by Schleicher (*137*), and a general review of the advantages and disadvantages of electrolytic separations by Ashley (*3*). Skowronski (*149*) has reviewed the history and development of the classical copper determination with the electric current, especially with regard to the assay of copper of high purity. Rogers (*131*) considers the peculiar difficulties in depositing radioactive elements from extremely dilute solutions in amounts capable of being detected only by their activity. The use to which controlled graded potentials may be put in electroanalysis, particularly where separations are to be effected, has been reviewed by Lassieur (*69, 70*) and Lingane (*75*). Lingane has concerned himself, in this paper and in a later (*76*) one, with the use of controlled potentials for coulometry and for separatory procedures with subsequent polarographic analysis. Kovalenko (*59*) in a study of "combined electrochemical methods" is likewise concerned with these complementary techniques. The application of electrography, internal electrolysis, and mercury cathode separations to methods of metallurgical microchemistry are briefly reviewed by Phillips (*125*). Other specialized reviews are referred to under the specific topics they cover.

THEORY

The peculiar conditions that surround electrochemical processes occurring during the procedures of electroanalysis have been the subject of special study by several analytical chemists. No attempt is made here to review the development of electrochemical theory as it applies to electrode processes, either in the general field of electrochemistry or in cognate branches of analytical chemistry. Rogers and Stehney (*132*) have found that the Nernst equation can be modified to describe the deposition of ions of very low concentration on an inert electrode. The kinetics and thermodynamics of electroanalytical determinations have been investigated by Schleicher (*138, 139, 141*). Haïssinsky (*42, 43*) has continued work begun earlier to elucidate the mechanism of deposition processes on a solid electrode by the use of naturally radioactive isotopes. He explains his results by postulating active centers on the electrode surfaces.

EQUIPMENT

A power unit designed to rectify an alternating current power supply for use in micro scale electrolysis has been described by Marion (*85*). Rabbitts (*127*) has described a six-unit stand for electrodeposition by which stirring is effected within the beaker by an iron slug sealed in glass and rotated by an Alnico magnet mounted outside and below the beaker. A "home-made" apparatus constructed of inexpensive materials for determining copper, nickel, silver, cadmium, and zinc in plating solutions was used by Langford (*68*). He used base metals for the cathode, as did Kovalenko (*56, 60, 61*), who employed anodized aluminum as a cathode.

A number of publications describe instruments for controlling the potential of an electrode during electrolysis. Lamphere has described two instruments (*66, 67*) for such a purpose, both useful where traces are being separated, but the newer instrument (*66*) is capable of producing higher currents or voltages up to 250 volt-amperes. Lingane and Jones (*77*) have built an instrument of this kind, from which unusual stability and good service may be anticipated. The circuit of Chambers (*19*) permits simultaneous control of several cells. Circuits depending on optical principles for balancing have been constructed by Kovalenko (*55, 58*) and Thomas (*153*). Perhaps the narrowest control may be obtained with the circuit developed by Penther and Pompeo (*124*), for which sensitivity of electrode changes of only 1 mv. is claimed.

A multipurpose instrument suitable not only for the control of electrode potentials but also for electrographic and coulometric electroanalysis and other electrical methods of analysis, has been reported by Lingane (*74*). Kovalenko (*57*) has a dual-purpose unit also usable for polarography. Allen's (*1*) apparatus for constant potential cathode reductions is especially designed for use with organic compounds, but may also be used for potential-current curves in concentrations too high for the usual polarographic instruments.

Reilley and coworkers (*130*) describe a simple three-tube constant current source for coulometric analysis, which may also be used as a constant voltage source.

Schleicher (*136*) has devised equipment for internal electrolysis by which 0.2 gram of copper, for example, may be deposited in only 3 or 4 minutes.

A substitute for the chemical coulometer of particular use in coulometric analyses is Lingane's (*78*) electromechanical integrator built around a ball and disk transmission. New developments in equipment for mercury cathode separations are mentioned below.

ELECTRODEPOSITION

Separations. The use of electroanalysis for separations of various types is widely applied (*3*). New directions for development continue to appear. Combinations of known electrical methods of analysis have lately begun to be studied, with the development of interesting possibilities. Kovalenko (*54*) employed polarographic determinations of lead and cadmium after the separation of large quantities of copper by electrodeposition, and also the polarographic determination of zinc after precipitation of cadmium on an aluminum electrode. The determination of copper by partial precipitation and weighing, completed by polarographic analysis of the remaining electrolyte for undeposited copper and other elements in brass, has been suggested (*142*).

Rhodium may be separated from iridium by controlled potential electrodeposition under conditions described by MacNevin and Tuthill (*83, 84*), but the deposit of rhodium is contaminated with oxide and cannot be quantitatively determined without first reducing it in hydrogen. Brouns (*11*) has studied the separation of cadmium and zinc with controlled potentials.

Mercury Cathode. An excellent review of the mercury cathode and its applications with 171 literature references has been prepared by Maxwell and Graham (*87*). Numerous modifications of the mercury cathode cell are designed to give easy separation of electrolyte and amalgam, faster deposition, and other special advantages (*5, 128, 133, 134, 143*). A means of continually renewing the mercury surface was used by Coriou *et al.* (*24*), who found it particularly useful for iron/zinc separation, and complete deposition of manganese and other reducible metals. Tsyb (*154*) separated iron from zinc at the mercury cathode in ratios as high as 10 to 1, using an elevated temperature. A means of cleaning the mercury for use in the cell is described by Massetti (*86*). A more elaborate apparatus available commercially for high speed separation of iron from electrolytes has been devised and tested by Center and coworkers (*18*).

Conditions for completely depositing mercury, nickel, cobalt, zinc, and iron on mercury have been investigated by Böttger (*9*).

It is not possible to mention all the procedures reported in the literature in which the mercury electrode is used routinely to effect separations. Among those of special interest has been its use on nickel alloys when magnesium is to be determined (*95*), on a solution of iron perchlorate preparatory to determining aluminum (*158*), on high temperature alloys preparatory to determining aluminum and titanium colorimetrically (*148*), and on bronzes preparatory to determining aluminum (*93, 94*). These latter papers by Mills and the paper by Coriou (*24*) include rate studies on the mercury cathode.

Internal Electrolysis. Schleicher (*140*) is alone among western analysts with his studies of internal electrolysis. These cover new methods for the precipitation of copper, nickel, cobalt, tin, and lead. Musha (*100, 101*) and Machida (*82*) have continued a series of papers on the application of various amalgams to the separation and determination of a number of elements under varying conditions. Chernikhov (*22*) and Kovalenko (*62*), respectively, have used internal electrolysis for the determination of tin in ore concentrates and in the presence of antimony and zinc. Kovalenko reports that antimony may be determined from the same solution by internal electrolysis. Mitroshina (*96*) employed internal electrolysis to determine small amounts of copper in iron. An improvement in technique claimed by Chernikhov (*21*) is the replacement of the semipermeable membrane around the anode by a film of collodion. Muraki has studied methods for depositing arsenic (*97*) and antimony (*98*) together with copper when analyzing manganese dioxide.

Coulometric Analysis. Coulometric analysis is the liveliest, most original, and consequently the most interesting aspect of current electroanalysis. Probably the first paper in this field was published in 1919 and development was slow until the last decade. Continuing the earliest developments has been Elema's (*30*) study of the determination of 10 to 100 micrograms of copper by first depositing from solution and then measuring the current generated when the copper is redissolved in a cell, as in the pioneer work of Zbinden (*161*). Kordesch (*53*) applied a similar technique to the determination of oxygen by measuring the current from an alkaline cell in which oxygen depolarized the carbon electrode.

Recently coulometric analysis has been extended to the generation of a number of titrating agents within a cell for direct titration—i.e., bromine for the titration of mustard gas (*144*), antimony (*12*), 8-quinolinol (*15*), and iodine (*160*); chlorine (*31*) and iodine (*129*) for the titration of arsenic; ferrous ion for the titration of cerium (*23*) and ceric ion for the titration of ferrous ion (*34*); and cuprous (*88*) ion for the titration of chromate and vanadate ions. Meier and Swift (*89*) report that an attempt to use dipositive silver ions as an oxidizing agent was unsuccessful. DeFord and coworkers (*26–28*) have devised means of preparing titrants outside the cell by quantitatively measured electric current, and this technique promises to open a new phase of coulometric analysis.

Another technique for determining halides (*80*) is the use by Lingane of a silver anode upon which the silver halides may be quantitatively deposited in proportion to the current passed. The halides alone, or in any combination but bromine and chlorine, can be individually satisfactorily determined.

Of considerable interest in commercial analysis is the determination of manganese, vanadium, and iron simultaneously by reduction at a cathode followed by an indicator electrode. This work is reported by Oelsen and Göbbels (*119*). The authors also found it possible to follow automatically the titration of sulfuric acid obtained when sulfur in steel was determined by combustion. Because of the war, this work appears to have been done independently of work reported in this country along somewhat related lines.

The microtitration of a series of weak organic acids from acetic to valeric has been accomplished in isopropyl alcohol solution by Carson (*16*). An advantage of the coulometric titration is that carbonate-free base need not be prepared.

Coulometric analysis requires accurate measurement of the amount of current passed in a determination. Two coulometers especially adapted to small currents have been devised by Bogan *et al.* (*10*) and Syrokomskiĭ (*152*). The first, like that of Lingane mentioned above, is mechanical, while the other, based on the electrode reactions of vanadyl ion, is chemical. Craig and Hoffman (*25*) of the National Bureau of Standards have found that the oxalate coulometer rivals the silver coulometer in accuracy.

Coulometry may often be applied to elucidate chemical processes. The reduction states of tellurium and selenium ions studied by Lingane and Niedrach (*79*) were established by these means.

Il'in (*48, 49*) used current density in an unusual way for the determination of the chromium content of plating baths. With increasing current density a potential break was observed, depending on the ratio of chromium to sulfuric acid if the temperature and cathode material were defined. Whether this phenomenon may be described as coulometric analysis is doubtful; its explanation is not clear and it may be more closely akin to that of polarography.

ELECTROSOLUTION

Stripping and Inclusions in Metals. While the earliest methods of electroanalysis were concerned with the precipitation of a material from solution on an electrode, the value of electrical methods for the dissolution of solid electrodes finally came to be realized. One well established industrial use is in determination

of the weight and/or thickness of plated coatings (*90*). Bendix (*6*) and Buser (*13*) have obtained patents on methods for determining the tin in a plated coating by electrolytic dissolution in standard iodine dissolved in hydrochloric acid. The iodine consumed is a measure of the tin dissolved. Saito (*135*) has compared the electrolytic with the chemical method for tin to the advantage of the former, especially when considerable copper is also present. All methods for measuring the thickness of tin coatings are reviewed by Price and Hoare (*126*). The chemical "jet" method has been combined by Ogarev (*120*) with the electrolytic for thickness measurements of a number of common electroplated coatings. A change in current may be used to detect penetration of the plating. Francis (*32*) used a constant current for successfully measuring the thickness of all common platings on steel, and tin, lead, zinc, and chromium on brass or copper. Gentry and Newson (*37*) also measured chromium plates by electrolysis in dilute sulfuric acid.

Some of the work of Klinger (*51*) in determining nonmetallic inclusions in metals has been mentioned but progress reports of his work have also appeared in the journal literature (*52*). Henkel (*45*) reports the electrolytic method is the best of eight methods for studying oxide inclusions in steel, but Klinger (*50*) did not find results for ferrous oxide (FeO) as reliable as with the chlorine method. Wada and Ishii (*156, 157*) have used the electrolytic method for inclusions in carbon steel and pig iron. A method (*47*) for discriminating and determining cementite and dissolved carbon in heat-treated carbon steels appeared last year.

Electrographic Analysis. The continued appearance of general articles relating to the use of electrographic analysis for testing metals (*150*) and minerals (*159*) is evidence that the usefulness of this relatively simple and inexpensive technique is still unfamiliar. A patent application (*14*) has been filed covering rather general use of the method.

In 1950 a symposium of the American Society for Testing Materials on the rapid identification of metals featured papers on the general use of the method (*46*), the identification of metal finishes (*72*), and the examination of plated and protective coatings for porosity (*36*). This last application represents a unique use of electrographic analysis and has been the subject of three other papers by Shaw (*145*) and Kronstein (*63, 64*).

Specific applications of the technique have been made by Levy (*71*) to the identification of high-temperature alloys, by Kumé and others (*65*) to the detection of alkali salts in filter paper, and by Miller (*91*) to the detection of copper.

Electro-oxidation and Reduction. The direct use of the oxidizing and reducing properties of anodes and cathodes in place of reagent chemicals as steps in a procedure continues to be studied on a limited scale. Murata *et al.* (*99*) used an anode to oxidize manganese for use in colorimetry. The cathodic reduction of uranium has been employed preliminary to titration with ceric ion (*29, 151*).

DETERMINATIONS BY ELEMENTS

Antimony. Norwitz (*108*) found that antimony may be successfully determined from an electrolyte containing sulfuric acid, hydrochloric acid, and hydroxylamine hydrochloride without critical temperature and potential control, although copper, cadmium, tin, arsenic, lead, bismuth, and silver interfere.

Bismuth. Bismuth may be quantitatively deposited on a copper-plated cathode at 90° C. from a tartaric acid–hydrofluoric acid electrolyte in the presence of tin, according to Goldberg (*40*). Arsenic, antimony, and copper interfere. Norwitz (*103*) determined bismuth after separation from interfering elements by deposition from a hydrazine sulfate–perchloric acid electrolyte.

Copper. An unusually interesting history of the assay of copper by electroanalysis has been referred to (*149*). Shikhvarger (*146*) has studied the separation and determination of minute quantities of copper, lead, and zinc obtained from air samples. Kovalenko (*56*) reports on the use of an oxidized aluminum cathode for determining copper in the presence of small quantities of cadmium. Notvest (*118*) has received a patent on an apparatus for simultaneously determining copper and lead in a solution stirred with carbon dioxide. Another contribution to the simultaneous determination of copper and lead from a perchloric acid electrolyte is by Goldberg (*38*), who reports a rapid method for analysis of silicon-aluminum bronze alloy.

In the presence of phosphoric acid, lead cannot be determined with copper, according to Norwitz (*107*), but he found that excellent separations can be made of copper from tin when both occur in brasses, bronzes, tin-base alloys, and aluminum alloys. He (*102*) also reports methods for determining copper in aluminum alloys when tin and antimony are both present, again using a phosphoric acid electrolyte, and for determining copper (*114*) in the presence of small amounts of bismuth or arsenic (*106*) using hydrogen peroxide in the electrolyte. He also reports a method (*113*) by which copper and arsenic are completely deposited on the cathode together from a solution containing hydroxylamine hydrochloride, the arsenic being present as an arsenide of copper.

Another study on the determination of copper in the presence of tin by the use of hydrofluoric acid is reported by Veitsblit (*155*). Copper may be deposited electrolytically when silver-copper alloys are analyzed by first separating the silver with ascorbic acid (*39*) or as chloride (*104*). In the latter case the interference of chlorides is prevented by the presence of a few drops of hydrogen peroxide. Norwitz (*110*) found that silver may be deposited cathodically in a satisfactory weighable form without potential control from an electrolyte containing sodium nitrite and nitric acid. A number of common elements do not interfere. Copper may be deposited from the solution after removal of the nitrite.

A procedure for determining copper electrolytically from perchloric-nitric acid solutions has been devised by Norwitz (*117*). He reports (*109*) that copper may be separated quantitatively from tin in a strong sufuric acid solution. Antimony deposits with the copper and must be separately determined (see lead and nickel).

Cadmium. Osborn (*121*) found that more satisfactory deposits of cadmium may be obtained from perchloric or sulfuric acid solutions containing a trace of gelatin. Separations may be effected from zinc or nickel by the procedure described, and the zinc deposited electrolytically after the removal of cadmium. Zivanović (*162*) used an electrolyte containing gelatin and boric acid for the determination of cadmium by internal electrolysis from a hot solution after the removal of interfering elements present in zinc concentrates by chemical means.

Cobalt. Llacer (*81*) has devised a microprocedure for determining cobalt by controlled potential deposition from solutions containing hydrazine as a depolarizer.

Iron. Haenny *et al.* (*41*) used a copper cathode on which to collect quantitatively radioactive ^{59}Fe. Norwitz (*116*) studied the deposition of iron from a phosphoric acid electrolyte.

Lead. Mention has been made of various lead determinations. Miller and Currie (*92*) describe a separation procedure for removing small amounts of lead from bronze alloys preparatory to gravimetric determination as the chromate. Haupt and Albrich (*44*) found that the anodic determination of small amounts of lead from pure cadmium was unsatisfactory because of contamination with thallous oxide. Norwitz (*115*) described a procedure for determining small amounts (0.5 to 2.0 mg.) of lead anodically using copper as a cathode depolarizer.

He also reports (*105*) on the determination of amounts of lead as high as 1 gram from a perchloric acid solution. Kovalenko (*60*) has studied the cathodic deposition of lead in the presence of zinc on his oxidized aluminum electrode, from which it is removed and determined polarographically.

Nickel. Silva Fangueiro (*147*) discusses methods for electrolytically determining nickel and copper from plating baths.

Selenium and Tellurium. Norwitz (*111*) reports a procedure,

claimed to be more rapid than earlier ones, for the separation of these elements by codeposition with copper. The actual determination is effected chemically.

Thallium. Besson (*7*) found that satisfactory results can be obtained for thallium by cathodic deposition on a liquid metal cathode but that the anodic determination is not quantitative. Haupt and Albrich (*44*) found that traces of thallium can be collected from pure cadmium satisfactorily on the anode from an ammoniacal electrolyte.

Tin. Lindsey (*73*) studied the recovery of 0.1 to 0.3 gram of tin from solutions of the stannous and stannic chlorides. Good recoveries are obtained if care is observed in washing the electrodes. Norwitz (*112*) employed the electrolytic separation of tin in the presence of hydroxylamine hydrochloride and sulfuric acid on redissolved precipitates of metastannic acid and sulfides.

Zinc. Patterson (*35, 122, 123*) found that zinc may be determined electrolytically in zinc-thorium alloys when more than 1% of zinc is present.

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Inorganic Gravimetric Analysis

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DURING the period under review (June 1950 to June 1951) significant contributions in the field of gravimetric analysis have come from three foreign laboratories. At the Institute of Obshchei, Pshenitsyn and coworkers recorded the results of an extensive investigation of determination of platinum metals.

At the Sorbonne, Dupuis, Duval, and coworkers contributed considerable data dealing with safe ignition temperatures of precipitates.

Rao and coworkers at Andhra University have materially increased the literature dealing with the determination of the earth elements of column four.

The number of organic precipitants used in inorganic analysis continues to increase; however, there has been relatively little progress in establishing relationships between structure and efficiency as a precipitating reagent. Out of such investigations might come many much needed specific reagents.

GENERAL PROCEDURES

Preparation of Samples and Precipitates. An automatic pipe-type sampler, suitable for coal, ores, fertilizers, etc., was discussed by Visman (*176*). Westwood (*182*) recorded precautions to be taken during sampling of pig iron and cast iron. The low temperature decomposition of various corrosion-resisting materials was discussed by Seelye and Rafter (*159*) and Rafter (*150*) Effective decomposition and more easily dissolved products were obtained by heating with sodium peroxide at 480° ± 20°. Iridosmine required four treatments. Except in the case of sulfide, the platinum crucible was not attacked. By fusing with sodium carbonate and sulfur Sarudi (*158*) converted arsenic, antimony, and tin into water-soluble products. Some copper passed into the aqueous extract, and if large amounts of arsenic were present there was some loss by volatilization. Martinez (*112*) stated that calcinations of the hydrates of iron and aluminum oxides could be replaced by infrared desiccation, although empirical factors were required to obtain the weights of metal, and the precision was poor. Lead dishes were used by Fainberg and Kedrova (*50*) in determining tin in poor ores and tailings. Proskuryakova (*136*) discussed accelerated filtrations of solutions containing silica. At pH less than 4 stable and easily filtered solutions were obtained.

Methods of Selective Separations and General Gravimetric Reagents. Galmés and Mataix (*70*) measured the pH at which the sulfides of cadmium, zinc, cobalt, and nickel could be precipitated. Zinc and cadmium were separated quantitatively at pH of 0.4.

Acridine in dilute acetic acid was used by Fidler (*54*) for the gravimetric estimation of vanadates, chromates, molybdates, and

tungstates. The yellow precipitates obtained at room temperature contained more water than precipitates obtained at the boiling point. The precipitates could be dried and weighed directly or ignited to oxide. Peltenburg (*131*) used pyridine to separate iron, aluminum, and chromium from zinc. The separation from chromium was imperfect. Rây and Bhaduri (*153*) used cystine in ammoniacal solution for the estimation of copper, cadmium, cobalt, nickel, and zinc. The precipitates were weighed directly. The separation of zinc from iron and aluminum was accomplished only by using a large excess of reagent in a tartrate or sulfosalicylic acid medium. Draney, Yanowski, and Cefola (*25*) found that the Cu^{++}, Ag^{+}, Hg_2^{++}, $PtCl_6^{--}$, Pd^{++}, and Au^{+++} ions in acidic solutions were precipitated by potassium dicyanoguanidine. The application of ammonium benzoate for the estimation of some of column four elements was described by Jewsbury and Osborn (*92*). Quantitative precipitations were obtained for tin(IV), titanium, zirconium, and thorium, and interference from many associated metals was avoided by the use of thioglycolic acid or salicyclic acid, or by controlling the acidity.

Gleu and Schwab (*76*) published a review dealing with the use of dithiocarbamates in place of hydrogen sulfide for the precipitation of metal ions. Haïssinsky and Yang (*79*) examined the stability of the oxalates, tartrates, and citrates of the metals of columns four and five. Their method was to determine the pH at the first appearance of a precipitate on adding hydroxide ion to solutions of the complexed metal. Borrel and Pâris (*13*) determined the stable heating ranges of the principal metallic precipitates of 8-quinolinol (8-hydroxyquinoline). The data obtained are contrary in some instances to the findings of other investigators. This is an important paper and should be examined by those interested in the analytical aspects of quinolinol. Precipitates of the following metals were examined: magnesium, copper, zinc, cadmium, manganese, nickel, cobalt, titanium, zirconium, vanadium, molybdenum, tungsten, thorium, iron, aluminum, and thallium.

The solubility products of the hydroxyquinolates of aluminum, magnesium, zinc, copper, and iron, and the effects of acidity and excess cations or anions were investigated by Tinovskaya (*167*). The application of pyramidone for the detection and determination of copper, zinc, cadmium, lead, bismuth, antimony, and the metal ions of column eight was discussed by Fungairiño (*66*). Colin (*20*) used modifications of Schoeller's tannin methods for the analysis of radioactive minerals. Procedures in outline form were described for the analysis of tantalum-niobium minerals, uranium in davidite and samarskite, titanium in complex minerals, and vanadium in roscoelite. The applications of thio-organic compounds as precipitating reagents have been extended further. Thioformamide (*69*) for arsenic and thioacetamide for arsenic, copper, cadmium, lead (*58*), and tin (*62*) are added to the already formidable list.

Analytical Methods for Specific Materials. The determination of copper sulfate in sulfide ores by diethyl dithiophosphate was described by Kakovskiĭ and Fedorova (*95*). Benzene was used to extract the copper precipitate; zinc could be determined in the aqueous layer. Emblem and Davy (*48*) determined silicon in silicon tetrachloride by esterifying the dioxane solution with absolute alcohol. The resulting silica gel was dried at 95° to 100° and ignited to silicon dioxide. A procedure for the sampling and analysis of tool and magnetic steels was recorded by Mazor (*114*). Young (*187*) published procedures for the determination of some two dozen elements in copper-refinery slimes. Jean (*89*) published the first installment of a review of the chemical analysis of siderurgical products. Baron (*4*) described procedures, which he preferred to carry out on separate samples, for the determination of water of constitution and of carbon dioxide in ferrous minerals.

Theories of Precipitation, New Aids, etc. West and Conrad (*181*) found that cation impurities tended to coprecipitate to a greater extent with organic precipitants. They suggested that the mechanism involved the flocculation of colloidal particles by electrolytes in the immediate zone of reaction. This was substantiated by the greater degree of coprecipitation of the trivalent cations, chromium and aluminum. The absorption of bivalent metals during the precipitation of hydrated oxides of iron, aluminum, and chromium by ammonia was discussed by Okáč and Bezděk (*128*). The experiments showed that some of the methods of separation were not quantitative even after several precipitations. Njegovan (*126*) purified precipitates of barium sulfate and ammonium magnesium and ammonium manganese phosphates by a process of dispersion and digestion. Beck (*7*) described a new gravimetric technique which was especially suitable for amorphous and gelatinous precipitates. The crucible was attached to a precipitating tube by a ground-glass joint and washing was accomplished by centrifuging. Automatic gravimetric analysis in inorganic chemistry was discussed by Duval (*43*).

LIGHT ALLOY ELEMENTS

Beryllium. Osborn (*129*) investigated the factors affecting the sodium carbonate fusion of beryl. Reliable results were obtained with a fusion ratio of two parts of sodium carbonate to one of beryl, while incomplete extraction with dilute phosphoric or sulfuric acids resulted if higher ratios were used. Qualitative and quantitative analytical methods for copper-beryllium alloys were studied by Séguin and Gramme (*160*). Systematic experimental comparison of the hydroxide, phosphate, and oxime methods indicated that the best results were obtained by precipitating beryllium as the phosphate after iron and aluminum had been removed as oximes. High values were always obtained when beryllium was precipitated by ammonium hydroxide.

From a critical study of several recommended procedures Quadrat and Švejda (*149*) selected the precipitation of beryllium by ammonium nitrite and its separation from aluminum by 8-quinolinol. A new method of separation was described which involved formation of an unstable alkali tartrate of beryllium while the aluminum complex remained stable. Přibl and Kucharsky (*134*) separated beryllium from aluminum in ammoniacal solution by forming a complex with the latter with ethylenediamine tetraacetic acid. Following destruction of the excess of the organic complex, aluminum could be determined in the filtrate. Furuhata (*67*) separated beryllium and aluminum by dissolving the latter in an alkaline medium. The small amount of dissolved sodium beryllate was reprecipitated on heating to 70°. A procedure for the separation of beryllium from iron and aluminum in the presence and absence of lithium, magnesium, and zinc was included (*68*). Minimum safe ignition temperatures for beryllium hydroxide obtained by seventeen methods were recorded by Dupuis (*27*).

Aluminum. For the direct determination of aluminum, Kassner and Ozier (*99*) used 8-quinolinol in an ammoniacal solution containing tartrate, cyanide, and hydrogen peroxide. Two methods for the determination of aluminum by anthranilic acid were described by Bhaduri (*10*). Mills and Hermon (*116*) determined aluminum in bronze by precipitation of the hydroxide subsequent to the removal of heavy metals by electrolytic separation with a mercury cathode. Bassett and Tomkins (*5*) described a procedure for the determination of aluminum in uranium-bearing material. Following removal of the acid sulfide cations, uranium was precipitated by 30% hydrogen peroxide. In this procedure precipitation of aluminum by ammonium hydroxide was preferred to the 8-quinolinol method.

Magnesium. Westwood and Presser (*183*) discussed the determination of magnesium in cast iron. Iron was removed by extraction with ether, and manganese by electrolysis; magnesium was precipitated as ammonium magnesium phosphate after the remaining elements were complexed with citrate. Hague and Shultz (*78*) also published a procedure for the determination of magnesium in cast iron. They claimed accuracies of the order of 0.002% magnesium in samples with the range of 0.01 to 0.10%

magnesium. After iron was removed by ether extraction, magnesium and some manganese were precipitated by addition of phosphate in ammoniacal citrate solution. Manganese was subsequently separated as the quadrivalent oxide. A procedure for the determination of magnesium in nodular cast iron was recorded by Yarne and Sobers (*186*); standard methods of separation and precipitation were applied. Valentin and Suchárová (*170*) separated magnesium from sodium and potassium by treating the solution of sulfates with hydrated silver oxide upon which magnesium hydroxide was selectively adsorbed.

NATURALLY RADIOACTIVE ELEMENTS

Thorium and Uranium. Venkataramaniah and Rao (*173*) stated that in nearly neutral solution thorium could be precipitated as $Th(IO_4)_4$. The precipitate could be weighed directly. In the presence of small amounts of cerite earths thorium was selectively precipitated from a 4 *N* nitric acid solution containing 3.5% periodic acid. Following the isolation of thorium and ceria earths from monazite, these authors (*171*) separated thorium by precipitation by sodium naphthionate. With 16 times as much ceria earths as thorium, a single precipitation sufficed. Venkataramaniah, Satyanarayanamurthy, and Rao (*174*) found that cerium and zirconium interfered in each of six methods for the determination of thorium. The precipitating agents were trimethylgallic acid; phenoxyacetic acid, benzoic acid, ammonium benzoate, tannic acid, and veratric acid. The last reagent gave slightly high results. For the separation of thorium from cerite earths, Rao and Rao (*151*) used *o*- and *p*-aminobenzoic acids. The precipitating medium was buffered on the acid side of Congo red. *o*-Chlorobenzoic acid was also used to precipitate thorium. Dupuis and Duval (*31*) recorded data on the thermogravimetry of twenty-four methods of precipitating thorium. Goyanes (*77*) reviewed methods for the detection and determination of thorium. Rodden and Warf (*154*) made a complete review of the analytical methods for uranium; detailed directions for its gravimetric determination as U_3O_8 were included. Organic reagents for the determination of uranium were discussed by Ware (*179*). Although not an ideal reagent, 8-quinolinol was considered to be the best of the gravimetric reagents. A manual of analytical methods for the determination of uranium and thorium in ores was published (*169*). Several standard gravimetric procedures for thorium are included.

ALKALI AND ALKALINE EARTH ELEMENTS

Sodium, Potassium, and Rubidium. The separation and determination of sodium oxide in the presence of lithium oxide, potassium oxide, and phosphorus pentoxide was investigated by Shell (*163*). The solution containing not more than 8 mg. of sodium was treated to precipitate $NaZn(UO_2)_3(OAc)_9.6H_2O$. Lithium salts and phosphates were selectively removed by hydrogen chloride–butanol. The residual sodium chloride was reprecipitated as the triple acetate. Miholič (*115*) confirmed the findings of earlier workers that ethanol could replace water of crystallization in sodium magnesium uranyl acetate. Jackson (*88*) recorded a new method for the determination of sodium in calcined alumina or its hydrate. After the sample was heated with hydrochloric acid in a sealed glass tube, the sodium was precipitated by zinc uranyl acetate reagent. Bourdon (*14*) found that in the precipitation of $K_2NaCo(NO_2)_6.H_2O$ it was desirable to use an empirical curve for each new lot of reagent. The ratio was seldom exactly two atoms of potassium to one of sodium and the amount of water also varied.

Belcher and Nutten (*8*) offered evidence to show that the ordinary two-solution reagent for potassium prepared in acetic acid by the method of Hamid (*80*) produced a precipitate whose composition was more constant than that produced by the Wilcox (*184*) method, which required sodium cobaltinitrite in nitric acid solution. However, in agreement with Wilcox, the results were high and required a factor of 0.97. An improved technique for the precipitation of potassium by sodium cobaltinitrite was recorded by Mason (*113*). Bourdon and Gielfrich (*15*) discussed the composition of cobaltinitrite complexes of potassium with and without other metals. A modified method for the isolation of potassium from fluoride and sulfate ions by an acid-alumina exchange-adsorption column was recorded by Dean (*22*).

d'Ans (*21*) provided a method for the extraction of rubidium from carnallites and its determination in the presence of potassium. By means of oxalic acid and a combined fractional crystallization, crystals of $RbH_3(C_2O_4)_2.2H_2O$ were obtained. After separation of the perchlorates and subsequent reduction, rubidium was determined by a chloride method.

Barium. During the period under review no researches on the gravimetric determination of calcium and strontium have been published.

Burriel and Caldas (*16*) found that the interference of the vanadate ion in the determination of barium could be eliminated by coprecipitation of vanadium with aluminum hydroxide. Iron and chromium hydroxide were less efficient.

STEEL FORMING ELEMENTS

Niobium and Tantalum. Hayashi and Katsura (*83*) found that the optimum pH for the formation of tantalum and niobium tannin complex was influenced by the presence of various alkaloids. Mixtures of brucine and tannin were considered to be the best precipitating reagents for the separation of tantalum and niobium. With tannin and cinchonine in oxalic acid solution at pH 1.6 all of the tantalum was precipitated while most of the niobium remained dissolved (*81*). Strychnine acted in the same way as cinchonine but was less effective (*82*). Bhattacharya (*11*) studied the effect of oxalate concentration and the acidity on the precipitation of tantalum and niobium by tannin. Separation of these elements in 2% ammonium oxalate could be effected in one operation, provided that the amount of tantalum oxide was at least 75% of the total oxides. Tannin was also used for the separation of tantalum and niobium in the presence of titanium, the latter being almost completely precipitated by tannin from ammonium oxalate at pH 4.0 (*12*). Gillis, Eeckhout, and Poma (*75*) separated niobium and tantalum with ferroin in hydrogen fluoride solution.

Titanium, Zirconium, and Hafnium. Various reagents, weighing forms, and safe temperature ranges for the determination of titanium were published by Dupuis and Duval (*33*). The iodate, 5,7-dichloro-, and 5,7-dibromo-oxine methods were recommended for automatic determinations.

Gavioli and Traldi (*72*) applied the mandelic acid method to the determination of zirconium in steels and cast irons. Good precision was obtained with synthetic mixtures and alloys containing 0.36 to 3.65% zirconium. Titanium did not interfere. According to Jonckers (*94*) the reactivity of mandelic acid is due to the $-CHOHCO_2H$ group. Nine compounds containing this group were as suitable as mandelic acid. Sarudi (*157*) recorded an interesting procedure for the separation of zirconium from iron, aluminum, thorium, and trivalent cerium. Disodium hydrogen arsenate in nitric acid medium was used to precipitate $ZrO.HAsO_4$. In the absence of excess of reagent the precipitate could be weighed as $(ZrO)_2As_2O_7$. Three procedures were included which accomplished the distillation from the precipitate of trivalent arsenic chloride followed by precipitation of hydrated zirconium oxide and ignition to the oxide.

Rao and coworkers used hydrazine sulfate (*175*), phthalic acid (*148*), tannin (*147*), and fumaric acid (*172*) for the precipitation of zirconium. Hydrazine sulfate could be used for the separation of zirconium from thorium at pH 2.8. Beryllium, nickel, and rare earths could be separated in the pH range 2.8 to 3.0. A single precipitation by phthalic acid in 0.35 *N* hydrochloric acid effected a separation from thorium, iron, aluminum, beryllium, uranium, manganese, nickel, and cerium earths. In the case of tannin the authors studied the effects of acidity with the hope of reducing a

positive error. Fumaric acid (*172*) in 0.25 *N* hydrochloric acid produced excellent precipitations of zirconium in the presence of interfering elements. The precipitate could be purified if necessary after dissolving in hot 6 *N* hydrochloric acid. Borrel and Pâris (*13*) recorded that 8-quinolinol with titanium or zirconium produced a mixed precipitate which was unsuitable for quantitative analysis.

Fujiwara published two procedures dealing with the determination of hafnium in the presence of zirconium. One method (*64*) involved a calculation from the weight of the mixed oxides and mixed pyrophosphates. In the second procedure (*65*) the mixed pyrophosphates were dissolved in hydrofluoric acid. Hafnium and zirconium were precipitated by sodium hydroxide, and treated with sulfuric acid and then the hafnium was largely separated by heating the diluted solution in the presence of hydrofluoric acid.

Vanadium. Duval and Morette (*44*, *45*) and Morette (*120*) examined existing gravimetric methods for the determination of vanadium. Seven acceptable precipitants and the corresponding safe ignition temperatures were recorded. Among other reagents, satisfactory results were not obtained by the barium vanadate, cobalt(III), hexammine, oxine, and the dicyanodiamidine methods (*120*). Fidler (*53*) stated that the compositions of the precipitates formed at room temperature by quinoline and vanadate were constant and independent of the quantity of reagent. Increasing the drying temperatures resulted in increased proportions of vanadium pentoxide. The composition of the precipitates formed by vanadate with quinine, strychnine, and brucine, under various conditions, were also recorded. Rasmussen and Rodden (*152*) precipitated vanadium as ammonium metavanadate and ignited to the pentoxide at 500°.

Molybdenum and Tungsten. Dupuis and Duval (*32*) recommended the oxinate for the automatic determination of molybdenum. They recorded also thirteen weighing forms and their temperature limits. Cinchonine was not considered a satisfactory reagent. Liang and Chang (*103*) reported on suitable ignition temperatures for the sexivalent oxides of molybdenum and tungsten and the determination of tungsten by alkaloids. Přibl and Malát (*135*) determined sexivalent molybdenum by quinolinol in an acetate-buffered solution of the disodium salt of ethylenediaminetetraacetic acid. Titanium, tungsten, vanadium, and uranium interfered. By varying the procedure slightly copper and iron could be determined. Myers, Shoebridge, and Guerin (*122*) published a method of analysis for tantalum-rich alloys. For the determination of tungsten the sample was dissolved in a mixture of hydrofluoric and nitric acids with a little sulfuric acid. The evaporated residue was fused with potassium carbonate, tantalum was removed as magnesium tantalate, and tungsten was recovered by the tannin-cinchonine method. A recipe was included for the treatment of the sample preliminary to the determination of molybdenum which was isolated as the sulfide and weighed as lead molybdate. The use of benzidine for the determination of tungstophosphoric anhydride in sodium tungstophosphate was discussed by Nazarenko and Shvartsburd (*125*).

Manganese and Rhenium. Dupuis, Besson, and Duval (*28*) stated that the only precipitates suitable for the automatic determination of manganese were the sulfate, oxalate, anthranilate, and oxinate. Pyrolysis curves for some other compounds were also recorded. Manganese monoxide was stable at 436° to 610°; and trimanganese tetroxide was found stable at 946° to 1000°. Njegovan and Morsan (*127*) published a procedure which produced pure ammonium manganese phosphate monohydrate.

Geilmann and Bode (*73*) found that in the absence of nitrates septivalent rhenium sulfide could be precipitated by sodium thiosulfate in 2 to 7 *N* sulfuric or 1 to 4 *N* hydrochloric acids. The precipitate could be dissolved by treatment with 10% sodium hydroxide and 30% hydrogen peroxide.

Iron, Cobalt, and Nickel. The separation of iron as basic formate from homogeneous solutions with urea was recommended by Willard and Sheldon (*185*). The precipitate was denser, more readily filtered, and adsorbed fewer impurities than the precipitate obtained by any other hydrolytic procedure. A modified two-stage precipitation effected excellent separations from bivalent metals. Gaspary Arnal and Miner Liceaga (*71*) extended the application of sulfates and sulfites to the determination of tervalent iron. Sodium sulfite in 60% ethanol was added to a neutral 60% ethanol solution of iron containing ammonium chloride. The precipitate was converted to and weighed as sulfate after final drying at 405°. Koszegi (*101*) found filtrations of hydrated iron oxide were improved if the hot iron solution was treated with ammonium hydroxide and later with a cold saturated solution of hydrazine sulfate. By complexing titanium with salicylate in the presence of ammonium carbonate Mannelli (*110*) was able to separate iron by precipitation as sulfide. Titanium was then determined by addition of ammonia. Similar separations of iron from manganese and thallium were recorded. Jean (*90*) published a bibliography of the chemical analysis of ferrous products.

Kallmann (*96*) precipitated cobalt as potassium cobaltinitrite. The addition of tartaric acid as a complexing reagent improved the scope and usefulness of the method. The modified procedure served as an excellent separation from virtually any combination of elements encountered in the metallurgical field. In the presence of large quantities of tantalum, niobium, and titanium which could not be held in solution by tartaric acid alone, hydrofluoric acid was of considerable value. In the precipitation of cobalt(III) hydroxide, Baker and McCutcheon (*3*) removed adsorbed alkali by dissolving the precipitate in hydrochloric acid, treating with hydrogen peroxide, and precipitating with trimethylbenzylammonium hydroxide. The thermogravimetry of cobalt precipitates was discussed by Duval and Duval (*47*). The anthranilate method was considered the best of all methods. The rejected methods were: molybdate, 1-nitro-2-naphthol, dinitrosoresorcinol, and dinitrosoorcinol.

These authors (*46*) also determined the safe heating ranges of nickel precipitates. It is of particular interest that the cyclohexanedione dioxime method was considered particularly efficient. Other preferred methods were iodide-iodate, anthranilic acid, and dimethylglyoxime. The rejected methods were sodium thiosulfate, salicylaldehyde, dicarbamidoglyoxime, diphenylglyoxime, α-furildioxime, zinc, and ammonia. Various publications (*93*, *132*, *178*) have dealt with interference of metal ions in the determination of nickel by 1,2-cyclohexanedione dioxime. Feinstein (*52*) recorded an additional procedure which avoided the interference of iron. Kurăs (*102*) used oxalendiamidoxime for the determinations of nickel. The reagent was water-soluble and the orange-yellow precipitate was weighed directly. Sapir (*155*) preferred hot aqueous solutions (85° to 90°) of dimethylglyoxime for the determination of nickel in steel. Ammoniacal solutions gave low results.

NONFERROUS ELEMENTS

Copper, Cadmium, Zinc, and Thallium. Sarudi (*156*) published a procedure for the determination of copper as copper(I) thiocyanate and its separation from arsenic and zinc. An excess of thiocyanate was found necessary. The purified precipitate could be dried at 100° to 180° and weighed. It was considered advisable to use a separate sample for the determination of arsenic. However, both arsenic and zinc could be determined in the filtrate from the copper(I) and thiocyanate precipitation; arsenic was removed as the sulfide and finally weighed as magnesium pyroarsenate; zinc was determined as ammonium zinc phosphate.

For samples containing no more than 100 mg. of cadmium, Denk and Denk (*23*) recommended the sulfide precipitation from perchloric or sulfuric acid solutions. The pure cadmium sulfide could be dried at 120° to 130° and weighed. Flaschka and Jakobljevich (*60*) used thioacetamide for the quantitative pre-

cipitation of cadmium sulfide. Zhivopistsev (*188*) used diantipyrylmethane to precipitate cadmium in the presence of copper, cobalt, nickel, aluminum, chromium, iron(II), and alkali and alkaline earth metals. The precipitate was dried at 110° to 120°. The thiosemicarbazone of salicylaldehyde was used by Hovorka and Holzbecher (*86*) to precipitate cadmium in solutions containing sulfate and nitrate ions. Chloride, fluoride, tartrate, and citrate prevented complete precipitation. Duval (*42*) published safe ignition temperature ranges for twenty-eight methods for the determination of cadmium.

Osborn (*130*) recorded a method for the determination of zinc oxide in zinc powder.

Murakami (*121*) used hexamminecobalt(III) chloride to determine thallium in chamber muds of sulfuric acid plants and in the flue dust formed during the calcination of ores. The procedure provided for the removal of lead, bismuth, tin, antimony, mercury, etc. Nakano (*123*) discussed the determination of thallium as cobaltinitrite.

Germanium, Tin, and Lead. Dupuis and Duval (*35*) recorded safe temperature limits for heating precipitates of tin. The cupferron method was considered best, while the benzenearsonic acid and tannin methods of precipitation were not recommended. These authors (*34*) published similar data for the determination of germanium. The cinchonine method was considered unsatisfactory. Selenous acid was used by Carvalho (*17*) for the precipitation of tin. Coprecipitation of titanium and cerium was prevented by the addition of hydrogen peroxide. Flaschka and Jakobljevich (*62*) found that thioacetamide could be used to precipitate tin sulfide, provided mercury(II) chloride was added to the suspension of the precipitate. The results were a little low. In the determination of tin in steels, Bagshawe (*2*) removed tin sulfide along with molybdenum(II) sulfide as a gathering agent. Finally iron was added to the solution of the above mixed sulfides, and this and the tin together were precipitated by ammonia.

Duval (*41*) recorded pyrolysis curves for all precipitates which have been proposed for the gravimetric determination of lead. For automatic determination, lead sulfide and the thionalide complex were considered the best of thirteen suitable methods. Dupuis (*26*) found that colloidal formation of lead tungstate prevented its use for gravimetric determinations. Flaschka and Jakobljevich (*61*) studied the precipitation of lead sulfide from acid and alkaline solutions by thioacetamide. Although the lead sulfide could be weighed after drying at 110°, conversion of the precipitate to lead sulfate produced more accurate results. Hovorka and Diviš (*85*) determined lead by α-isatin oxime. The blue precipitate was dried at 105° to 110° following a treatment with ethanol and ether. In the analysis of fusible alloys Etheridge (*49*) found that fuming at 250° eliminated contamination of lead sulfate by bismuth, but at 350° to 400° contamination became significant.

Arsenic, Antimony, and Bismuth. Chernyĭ and Podoinikova (*18, 19*) determined arsenide-sulfide minerals in sulfide and arsenosulfide ores by differential thermal decomposition. Two samples mixed with aluminum oxide were heated at 400° and 500°, respectively. The boat residues were analyzed for nickel, cobalt, and sulfur and the difference between the two sets gave the proportion of these metals present as arsenosulfide minerals. To precipitate trivalent or quinquevalent arsenic sulfide Gagliardi and Loidl (*69*) used thioformamide, and Flaschka and Jakobljevich (*59*) used thioacetamide. Dupuis and Duval (*37*) recorded safe ignition temperatures for arsenic precipitates. They rejected the xanthogenate, uranium arsenate, and molybdoarsenate methods.

Thioacetamide was also used by Flaschka and Jakobljevich (*59*) for the determination of antimony. Either the black or red sulfide could be used, although the former was more convenient and accurate. The red precipitate was dried in carbon dioxide at 280° to 300°; the black modification was dried at 120°. The thermogravimetry of antimony precipitates was studied by Morandat and Duval (*119*). The thiocyanate was considered the best of all methods. Tannin and 8-quinolinol were considered to be unsatisfactory precipitants.

Majumdar and Sarma (*108*) stated that under suitable conditions benzenearsonic acid could be used to precipitate bismuth free of zinc, manganese, nickel, cobalt, lead, mercury, thallium, sulfate, alkalies, and alkaline earths.

RARE EARTH ELEMENTS

The precipitation of rare earth elements by ammonia and oxalic acid as applied to minerals was discussed by Serebrennikov (*162*). In the presence of much iron and aluminum the oxalate method produced low results and the fluoride method should be used. A recommended alternative was outlined. Beck (*6*) stated that scandium produced a salt insoluble in mineral acids with aneurine pyrophosphate, and with adenosine triphosphate a salt insoluble in acetic acid. Zirconium was the only interfering element. Dupuis and Duval (*30*) determined pyrolysis curves for gadolinium oxide.

THE NOBLE ELEMENTS

Silver and Gold. A new organic precipitant for silver was recorded by Tarasevich (*165*). The bromine derivative of benzo-1,2,3-triazole precipitated silver in the form of $C_6H_3BrN_3Ag$, which was stable to heat and light, and insoluble in aqueous ammonia, organic solvents, or dilute acids. Determinations could be made in the presence of copper, nickel, bismuth, thallium, lead, and chlorine. Directions for the preparation of the reagent were included. Wenger (*180*) recorded a new gravimetric reagent for silver and copper. 1-Nitroso-2-naphthol precipitated silver at pH 8.5 in the presence of a borax–boric acid buffer. The copper compound was precipitated at pH 5.6 in the presence of an acetic acid–sodium acetate buffer. The precipitation of silver chloride from perchloric acid solutions and other mineral acids was discussed by Mills and Hermon (*117*). Marin and Duval (*111*) recorded safe ignition temperature limits for precipitation forms of silver. A new compound, $HOCH_2.NAg.CH_2OH$, formed by precipitation by formaldehyde and ammonia was recorded.

Malowan (*109*) used morpholine oxalate to precipitate gold. Nitric acid interfered.

Platinum Metals. Vořišek and Vejdělek (*177*) used the hydrazide of *m*-nitrobenzoic acid for the determination of palladium. In mineral acid solutions only gold interfered, but in neutral solution the reagent also precipitated mercury (II), copper, iron, nickel, molybdenum, platinum, and osmium. The precipitate was finally ignited to palladium. Jackson and Beamish (*87*) examined in detail the platinum sulfide precipitation. High results always attended the formation of sulfide from solutions of sodium hexachloroplatinate, but very accurate results were obtained in the absence of complexed sodium chloride. The retention of sulfur in platinum sulfide did not account for positive errors. Hill and Beamish (*84*) examined the efficiency of chlorination of iridium and iridosmine.

A considerable amount of work on the determination of platinum metals has been recorded by Pshenitsyn and coworkers. Of ten publications, five deal with the analysis of copper-nickel slimes. In general, the methods involve the application of well-known procedures. For the collection of palladium and platinum, acetylene was used by Pshenitsyn, Ginzburg, and Sal'skaya (*143*). The method was considered accurate to within 1.5%. The calomel method was used for the same purpose by Pshenitsyn and Yakovleva (*146*). There were no interferences from copper, nickel, iron, iridium, or rhodium. Precipitation as ammonium chloroplatinate and chloropalladate was used by Pshenitsyn and Gladyshevskaya (*144*). The platinum metals were selectively extracted by treatment with aqua regia. Perhaps the most significant of the five reports (*145*) described the selective extraction of the base metals from the slimes by fusion with borax at 1200°. Lead and silica were removed from the platinum metals

residue by conventional procedures. Attempts to collect platinum and palladium in the flux by means of a silver button failed. Pshenitsyn and Fedorov (*139*) determined ruthenium in slimes by a procedure which involved the initial removal of base metal impurities by standard procedures followed by a series of fusions, then reduction by alcohol to isolate ruthenium and other platinum metals. Fusions with sodium carbonate and subsequent reduction with zinc or magnesium produced ruthenium with traces of platinum; the latter could be removed by leaching with aqua regia. This procedure seems somewhat cumbersome. Procedures for the separation of rhodium from iridium were also recorded by Pshenitsyn. Chromium(II) chloride (*138*) was used to reduce rhodium to metal. This procedure will involve the subsequent difficult separation of iridium and chromium. The second procedure (*140*) is an application of the lengthy procedure originally described by Gibbs in 1863. Pshenitsyn and Ginzburg (*142*) used zinc oxide for the hydrolytic separation of platinum metals. The hydrated oxides were contaminated by platinum and two or more precipitations were necessary for its removal. Excess zinc oxide also resulted in adsorption of platinum. In the separation of platinum from iridium, chlorine was used as the oxidizing reagent. Reviews of methods of analysis of the platinum group metals were also published by Pshenitsyn (*137*) and Pshenitsyn and Ginzburg (*141*).

New rapid methods for determining platinum metals in concentrates and mattes and nonsiliceous ores were developed by Seliverstov (*161*). Hot sulfuric acid extacts were treated with sulfur and the resulting sulfides were roasted, litharge, silica, etc., were added, and the mixture was subjected to fire assay. The silver–platinum metals bead was treated by known methods. An alternative procedure, applied to rich ores, etc., involved continued wet treatment of the oxidized residue by adaptations of standard methods. For the separation of small quantities of rhodium in platinum catalysts Ubaldini (*168*) treated the aqua regia extract with ammonium acetate and formic acid to produce a precipitate of rhodium and platinum from which the rhodium was isolated by fusion with potassium pyrosulfate.

NONMETALLIC ELEMENTS

Boron, Carbon, and Silicon. Duval (*40*) investigated the ignition temperature limits for gravimetric precipitates used in the determination of boron. Nitron fluoborate was recommended for the automatic determination.

Majumdar (*106, 107*) recorded methods for the analysis of adulterated graphite. Complete combustion of volatile matter and adulterants such as charcoal, coal, and coke required 5 to 20 minutes. Errors of less than 2% were obtainable. The determination of carbon in steel was discussed by Popova and Rybina (*133*). A procedure was included to obtain the total carbon and the free carbon in the carbide.

Dupuis, Besson, and Duval (*29*) recorded ignition temperature limits for ten silicon precipitates, eight of which were suitable for automatic methods. A procedure for the extraction and determination of silicon in aluminum and its alloys was published by Berthier (*9*). The alloy was amalgamated by mercury in a sulfuric acid solution. Following removal of the latter, the aluminum was dissolved by concentrated hydrochloric acid and the silicon was precipitated by dilution. Dodero and Rambeaud (*24*) recorded some improvement in the procedures for the determination of silicon in chromium steel. Aubry and Turpin (*1*) treated iron ores with an acetic acid–sodium acetate mixture. To determine silica the residue was selectively extracted with sodium sulfide, then with hydrochloric and nitric acids. In the determination of silicon in ferrous alloys, Jenkins and Webb (*91*) obtained precise and accurate results through the use of gelatin. Nardell (*124*) isolated dodecatungstosilicate by precipitation by benzidene.

Phosphorus. Frey (*63*) studied the relative rates of molybdophosphate precipitation and the formation of polymolybdate as a function of temperature, ratio of molybdate excess to nitric acid, amount of ammonium nitrate, stirring rate, and total volume. While variations of volume had little effect, increasing any of the other variables resulted in increasing both the rate of precipitation and the polymolybdate formation. Two methods of precipitation were described. Templeton and Bassett (*166*) recommended precipitation by ammonium molybdate as the most accurate method for the determination of phosphate; the precipitate was dissolved in ammonium hydroxide, converted to ammonium magnesium phosphate, and ignited to the pyrophosphate. In some cases phosphate was precipitated as ammonium uranyl phosphate ($UO_2NH_4PO_4$) and weighed as uranyl pyrophosphate.

The degree of interference of arsenic in the determination of phosphorus in steels was investigated by Kitahara (*100*). The error in the phosphorus values owing to arsenic in excess could be minimized by precipitating ammonium molybdophosphate below 45° and washing with ammonium nitrate and nitric acid solution at 10° to 15°. Mager (*105*) described a procedure for the determination of total phosphoric acid in phosphates. Kassner and Ozier (*98*) extended the analytical usefulness of the double-strength citromolybdate solution to include the determination of phosphorus in alloys. Kanevskaya (*97*) recorded a procedure for the rapid determination of phosphorus in iron ore essentially free of titanium, arsenic, and vanadium. Dupuis and Duval (*36*) investigated ignition temperature limits for phosphorus precipitates. A detailed study was made of the precipitation by molybdic acid reagent.

Sulfur. Precipitants, weighing forms, and ignition temperature limits for the gravimetric determination of sulfur and its organic derivatives were discussed by Dupuis and Duval (*39*). Fischer and Sprague (*56*) found that the incomplete precipitation of benzidine sulfate in the presence of foreign ions was more probably the result of imperfect crystal formation than of increased solubility. Figurovskiĭ and Ushakova (*55*) examined methods of regulating the dispersion of barium sulfate by addition of picric acid, pyridine, salicylic acid, etc. Liang and Hsu (*104*) stated that the tendency of manganese, cobalt, and nickel ions to coprecipitate with barium sulfate in 0.2 *N* acid was almost negligible. Milner and McNabb (*118*) recorded a procedure for the determination of sulfur as barium sulfate in the presence of ferric ion. The former was first precipitated in the presence of ferric hydroxide, then filtered after addition of excess hydrochloric acid. With more than 200 mg. of iron, contamination became significant. A method for the determination of sulfur in zinc blende by oxidation by hydrogen peroxide in an oxalic acid medium was recorded by Fehér and Heuer (*51*). The oxides of sulfur were distilled into ammoniacal hydrogen peroxide and subsequently determined as barium sulfate. A procedure for the determination of sulfur trioxide in liquid sulfur dioxide was described by Steinle (*164*). A frozen mixture of barium chloride and formalin was added to liquid sulfur dioxide previously chilled by dry ice.

Halogens. Georch (*74*) studied the determination of fluorine by precipitation of lead chlorofluoride by lead chloride.

Dupuis and Duval (*38*) recorded pyrolysis curves for precipitates used in gravimetric determinations of halogens, either as simple or complex ions.

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Inorganic Volumetric Analysis

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THIS review covers the years 1950 and 1951 and follows the pattern of previous reviews.

The trend toward instrumental methods has been quite pronounced in the past few years, with the result that developments in direct volumetric methods have been decreasing to a noticeable extent.

BOOKS AND REVIEWS

Re-edited methods for ferrous and nonferrous metals by the American Society for Testing Materials (*2*) have brought this useful volume up to date. Books and pamphlets on the assay of uranium include one containing a review of methods used on the Manhattan Project (*186*), a handbook of methods in use in England (*40*), and one in use in the United States (*187*). A new edition of the well-known monograph on volumetric iodate methods has appeared (*203*) and a comprehensive review of sampling methods (*56*) was published. Reviews include those on fluorine (*76*); Kjeldahl nitrogen method as applied to microanalysis (*123*); the determination of carbon dioxide from carbonates in agricultural and biological material (*227*); and the determination of chlorine in water (*105*). Reviews on the Karl Fischer method for water have included comparison and preparation of reagents and methods of determinations (*114*), a round table review discussion (*150*), and applications to determination of water in minerals (*149*).

STUDIES OF METHODS

Studies of titration in glacial acetic acid have shown that salts of strong bases and weak acids, weak bases and weak acids, and weak organic bases can be titrated using perchloric acid as a titrating agent (*142*). The relative merits of ceriometry and vanadiometry have been studied and ammonium vanadate is stated to have certain advantages (*232*). Manganese sulfate is stated to have certain advantages over iodine monochloride as a catalyst in ceric sulfate titrations (*239*).

Factors affecting the stability of ferrate(VI) ion in aqueous solutions have been studied to improve the use of the reagent as an oxidizing agent in alkaline solutions (*195*). During titrations in neutralization reactions the change in volume and also heat of the reaction has an effect on the pH of the solution. Changes in internal resistance are indicated (*193*).

APPARATUS

Considerable interest has been shown in the development of instruments for high frequency titrations. Of the various instruments described (*5, 21, 23, 92*), the stable high frequency titrim-

eter (*23*) and the impedance measuring circuit made from commercially available parts (*92*) appear quite satisfactory. A high-frequency apparatus from Japan (*157*) and the radio-frequency apparatus for conductometric titrations (*26–28*) are of considerable interest. The radio-frequency equipment can be used for microtitrations. A simple apparatus for microconductometric titrations of volumes less than 1 ml. has been described (*208*).

Improvements in apparatus for the Karl Fischer titrator have been in a microburet (*243*) and a magic-eye indicator (*120*). A dark chamber for use in a chemiluminescent indicator titration with highly colored solutions has been described (*119*). A cell for photometric titration has been made (*87*). Construction and details have been given (*111*) for an inexpensive recording autotitrator. Modifications of volume measuring equipments have included a platinum tip for a microburet (*42*); a constant-flow buret based on a Mariotte-flask principle (*225*); a 1-ml. buret made from a pipet (*209*); a microburet (*129*); a buret for use with air-sensitive reagents (*16*); a combination buret and Jones reductor (*65, 68*); filling devices (*91*); a microburet-pipet combination (*185*); and a micropipet (*32*). For microtitrations, a device for rotating the vessel has been described (*210*).

STANDARDS AND REAGENTS

A series of papers in *Metallurgia* (*162–164*) has reviewed the subject of primary standards for various types of reactions, including acidimetry, oxidimetry, and argentometry. Potassium acid phthalate is recommended (*199*) as a standard for acidimetric titrations in glacial acetic acid. A color standard has been used for precision assay of potassium acid phthalate (*57*). The following have been suggested for use as acidimetric standards: hydroxymethylaminomethane as a substitute for potassium acid phthalate (*74*); sulfamic acid (*100*); and potassium iodate (*9, 166*). An investigation has been made on the standardization of permanganate (*55*), and a rapid method for making a standard permanganate solution (*248*) using kaolin has been proposed. Commercial analytical reagent potassium dichromate is shown (*137*) to be satisfactory as a standard.

The standardization of titanium chloride solution with potassium dichromate (*34*) has been suggested as better than other methods. Manganese(III) solutions can be preserved for at least 10 days (*107*) and chromous salts can be kept when in contact with amalgamated zinc (*154*). The reductor buret was used for vanadium(II) solutions (*145*). A study of the standardization of hypochlorite solutions (*133*) shows Penot's method with arsenite to be the most satisfactory. The use (*216*) and preparation (*217*) of periodate solution has been described and another method for preparing sodium thiosulfate has been given (*240*). A detailed description of volumetric standardization (*4*), based on pure electrolytic silver as ultimate standard and with iodine, sodium carbonate, sodium chloride, arsenious oxide, and potassium dichromate as working standards, is given by the Analytical Chemists Committee of Imperial Chemical Industries, Ltd. A study of the standardization of silver nitrate for the assay of cyanides has been made (*103*).

In the Karl Fischer titration, sodium tartrate dihydrate is proposed as a primary standard (*156*). By adding starch and potassium iodide together (*207*), a more stable indicator solution is obtained. Silver peroxide is proposed as an oxidizing medium for cerium determinations (*122*).

DETERMINATIONS BY ELEMENTS

Acids. Mixtures of two weak acids were determined by conductance titration using empirical conditions and formulas (*194*). Free acids were determined in antimony and bismuth salt solutions by precipitating with potassium ferrocyanide, filtering, and titrating with sodium hydroxide (*170*). Potassium oxalate is used to complex aluminum in determining free acid in aluminum nitrate (*25*). In a novel method, sulfuric acid is precipitated in aniline and, after filtering and dissolving, is titrated with sodium hydroxide (*169*). For traces of sulfuric acid in the air, collection on filter paper is used, followed by titration as usual (*141*).

Aluminum. Variations of the fluoride method were: using lithium chloride in a routine control method (*86*); saturating the solution with sodium chloride in ethyl alcohol prior to titration (*184*); and using barium hydroxide and barium salts prior to addition of the potassium fluoride (*231*).

Antimony. Low's permanganate method is used in the analysis of bearing metals (*181*). Antimony is determined together with arsenic by titration with potassium bromate (*173*). A modification of the method of Györy is given in which complete decomposition of hydrogen peroxide, used for alloy solution, is ensured by decomposition with sodium sulfite, followed by reduction with sulfur dioxide and titration with potassium bromate using methyl red as an indicator (*19*).

Arsenic. Arsenic is determined iodometrically in the eluate from an ion exchange column which separates oxidized arsenic from interfering elements (*165*). A simplified distillation apparatus for separation of arsenic is described and the addition of phosphoric acid is recommended in a potassium bromate titration with methyl red indicator which is decolorized at the end point (*15*). In mixtures of arsenic and antimony, arsenic is titrated preferentially by potassium bromate in the presence of iodine monochloride. Too much sulfuric acid interferes and should be neutralized (*173*).

Arsenic is determined in iron, steel, and iron ores by addition of copper sulfate to the solution, reducing the arsenic with sodium hypophosphate, and filtering. Excess standard iodine solution is added to the filtrate and the excess is titrated with 0.03 *N* sodium thiosulfate using starch as indicator (*115*).

Barium. Standard sulfuric acid is added to an aqueous solution, followed by titration of excess acid with sodium hydroxide (*54*).

Beryllium. The high-frequency titrimeter was used for titrating an essentially pure solution of beryllium with sodium hydroxide (*5*).

Boron. Boron in electroplating baths (*247*) and magnesite (*99*) was determined by the usual volumetric method employing mannitol after removing metals. Metal borides are fused with sodium carbonate and, after dissolving and filtering, titrated with sodium hydroxide as usual (*30*).

In a rapid method, sodium carbonate replaces the usual sodium hydroxide (*134*).

Bromine. A study (*6*) of bromometric titration reports on the development of an apparatus which eliminates bromine losses due to evaporation, uses titration with sodium and potassium thiosulfates, and gives an iodometric end point for titration of bromine.

In a comparison study (*98*), the method of Kolthoff and Yutzy, in which the bromide is oxidized with sodium hypochlorite, was found most satisfactory. Its application to mixtures of chlorides and bromides is described (*97*). Compared with it is an electrolytic method of oxidation, and the aeration method of Evans in which chromic acid was found to be a more selective oxidizing agent than sulfuric–chromic acid (*98*).

In the determination of bromine ion, most interferences can be removed by sodium carbonate treatment. Bromine can also be distilled into alkaline hydroxide after treatment with potassium permanganate. A thiosulfate titration is made following the addition of chlorine and potassium iodide (*220*).

In Meulen's method of oxidation with potassium oxychloride the pH should be kept between 6 and 7 and addition of sodium chloride should be omitted (*180*). Bromine can be determined in the presence of large amounts of chloride and iodide by removing iodine following addition of ferric ammonium sulfate and titrating with chlorine water in slightly acid solution (*222*).

Cadmium. A rapid iodometric method which has several interfering ions has been proposed (*3*).

Calcium. The high-frequency titrimeter has been used for titrating calcium with a soap solution but magnesium interferes (*113*). Variations of the time-honored oxalate-permanganate method have been reported for potassium minerals (*1*) in the presence of nickel and cobalt (*81*), in dolomites and slags (*234*), when using acetic acid (*235*), and after first separating with oxine followed by an oxalate precipitation (*190*). Calcium can also be separated with potassium ferrocyanide and the precipitate titrated with permanganate (*70, 71*) or ceric sulfate (*72*). Versene has been used for the analysis of leaf tissue (*245*). By using a 0.1 *N* solution of hexanitrodiphenylamine, calcium can be determined volumetrically but phosphate, carbonate, and ammonium ions interfere (*75*).

Carbonate. Several methods are enumerated for the determination of carbonate in agricultural and biological materials. These are mostly modifications of titrimetric methods in which carbon dioxide is absorbed in standard alkali solutions and titrated with acid (*227*).

Carbonates are determined in the presence of bromine and chlorine by reducing the halogens with ferrous sulfate and sodium arsenite, boiling out the carbon dioxide into an alkaline solution, and titrating (*97*).

Cerium. A "silver peroxide" has been used in the oxidation of cerium which is more efficient than persulfate and silver ion (*122*).

Chlorine. Alkali halides and amine hydrochlorides can be titrated with perchloric acid in glacial acetic acid (*101*). By masking the premature blue color, the mercuric nitrate–diphenyl carbazone titration was improved (*46, 47*). Modification of the Volhard method was applied to inorganic salts after liberating chlorine with manganese dioxide and absorbing in sodium carbonate and peroxide (*112*); to iodates after precipitation as bariumio date (*206*); and to bromine-containing substances (*197*).

If the ferric ion concentration is made 0.2 volume formal, Volhard end points are stable (*213*). A review of methods for chlorine in water showed the iodometric and methyl orange titration methods to be satisfactory (*105*).

In a rapid method for hypochlorite, potassium iodide is used as titrant (*168*). In the Berg method, accuracy is improved by keeping the acid concentration within certain limits (*238*). The direct titration with mercuric nitrate using high-frequency titration appears superior to the potentiometric or conductometric method (*22*).

Chromium. In alkaline solutions, potassium ferrate has been used to oxidize Cr(III) (*197*). Variations of the ferrous sulfate–permanganate titration for chrome ore (*200*), synthetic samples (*94*), and in the presence of vanadium (*78*) and steel (*110*) have been made.

For cast iron and steel, a modification of the bromate oxidation proved highly satisfactory (*96*). An iodometric method for a mixture of permanganate and dichromate employing reduction of permanganate with ethyl alcohol has been proposed (*83*).

Cobalt. In an iodometric method the carbonate complex of Co(III) is reacted with iodide to form iodine (*132*). By adding excess ferricyanide to a solution, cobalt can be determined after back-titrating with standard cobalt sulfate (*229*).

Columbium. A study of the reduction with zinc amalgam followed by permanganate titration has been made (*127*).

Copper. Several procedures are reported which use iodometric titrations (*7, 35, 181*). In one instance sulfide ores are oxidized with perchloric acid and complexed with fluoride before the iodometric titration (*89*).

Two methods are reported for titration with potassium permanganate of the ferrous ion that results from the oxidation of cuprous oxide (*241*) or cuprous sulfide (*172*).

In the bromometric titration of hydrazine following the precipitation of copper with hydrazine sulfate, fuchsin, tropeolin OO, or thymol blue are recommended as indicators (*177*).

A new method is reported in which copper thiocyanate is precipitated with pyridine and ammonium thiocyanate, and the excess thiocyanate is titrated with silver nitrate (*167*).

Cyanide. A silver nitrate titration can be performed in a photoelectric colorimeter or turbidimeter in the presence of ammonia and potassium iodide (*13*).

Nickel ammonium sulfate can be used to titrate cyanide using dimethyl glyoxime as indicator (*233*).

It is recommended that the silver nitrate solution used for titrating cyanides be standardized by the Volhard method (*103*).

Ferrocyanide. In a variation of a standard procedure, potassium ferrocyanide is determined by titration with zinc sulfate, with ferric chloride as outside indicator, and without potassium chloride added (*102*).

Sodium vanadate with diphenylbenzidine as indicator can be used to titrate solutions which are not more than 0.0166 *N* in ferrocyanide and are over 1 *N* in H^+ (*179*). Results are reported to be as accurate as with potassium permanganate and can take place in the presence of hydrochloric acid and oxalic acid.

Fluorine. A photofluorometric method using thorium nitrate and quercetin as fluorescent indicator has been proposed (*244*).

The method of Willard and Winter has been discussed (*8, 85*) and a simplification applied to agricultural substances (*84*). The back-titration method has not proved as fast (*202*) as the salt-acid method of Williams. By titrating in a 50% alcohol system using gallocyanine as an indicator, usual errors may be avoided (*183*).

A modification of the lead bromofluoride method has been applied to the analysis of welding flux (*45*).

Germanium. Germanium dioxide reacts with mannitol to form a strong complex acid which can be titrated with sodium hydroxide (*48*).

Iodine. Iodine in thallium salts is determined by reducing the thallium to the metallic state with zinc and titrating the iodide potentiometrically with silver nitrate (*126*). A means of improving the accuracy of mercurimetric titration with dithizone indicator is suggested (*230*). Permanganate titrations are carried out in the presence of sulfuric acid and acetone, a complex being formed (*43*). Iodometric titrations are made following oxidation to the iodate by chlorine water (*180, 222*). Free iodine is determined in the presence of iodides by titration with alkaline arsenious oxide solutions and then total iodine is determined after adding potassium iodate and again titrating with arsenious oxide (*82*).

Iridium. After oxidizing, the sample is titrated with hydroquinone or potassium ferrocyanide using *o*-dianisidine as an indicator (*146*).

Iron. Metallic iron is determined in the presence of its oxides by dissolving with bromine in alcoholic solution and filtering. Iron from both oxide and metal is determined by the Zimmermann-Reinhard method and Fe^{+2} is determined by permanganate (*237*). Metallic iron in ores is also determined by permanganate titration following solution with copper sulfate (*205*). Direct titrations of ferric iron include those with mercurous nitrate (*67, 236*), with stannous chloride (*196*), with a double indicator of thiocyanate and ammonium molybdate (*221*), and with titanous chloride (*11, 69*).

In another method, the sample is dissolved in a solution containing ammonium vanadate, and the unreduced vanadate is titrated with Mohr's salt (*109*). Ti^{+3} is also used to titrate iron hydroxyquinolate (*10*). Ascorbic acid is used to titrate Fe^{+3} (*73*) and it is also added in excess and back-titrated iodometrically (*175*).

Methods involving reduction of iron followed by titration employ potassium dichromate (*37, 160*) and ceric sulfate (*196*), the latter in the presence of ethyl alcohol and acetaldehyde (*224*), and in a micromethod (*66*) following reduction with zinc amalgam.

In a modification of Densen's method, an improved decomposition chamber is described and direct permanganate titration is replaced by an indirect titration (*95*).

Representative volumetric methods are given on a semimicro scale (*189*).

Lead. As an indicator in the titration of lead with molybdate, potassium cyanate and stannous chloride are used, which form the red $K_3[Mo(CNS)_6]\cdot 4H_2O$ (*131*). Precipitation as oxalate followed by oxidimetric titration of the oxalate is stated to be more precise than the chromate-iodometric method (*64*). For ores and concentration products the chromate method is used (*60*). Lead oxide in the presence of lead is determined by heating with ammonium chloride and titrating the ammonia liberated (*20*).

Magnesium. Magnesium in leaf tissue has been determined using Versene (*245*). High-frequency titrations with soap solutions have proved satisfactory in the absence of calcium (*113*). Oxine precipitation followed by bromide titration has been used after a ferrocyanide separation (*70*). Oxine has also been used as a final separation for magnesium in cast iron (*44*). An arsenate-cerimetric method has been proposed (*144*). Adaptations of the magnesium ammonium phosphate method have been made for rapid methods in dolomite and slags (*234*), potassium minerals (*1*), and agricultural products (*93*).

Manganese. Manganese can be determined in strong alkaline solutions by titrating with potassium ferrocyanide in the presence of ammonium carbonate and potassium cyanide (*229*). A study of the ferrocyanide method showing effects of interfering elements has been made (*174*). When oxidizing manganese with persulfate, silver consumption can be cut by proper attention to acid concentration (*51*).

Manganese in a mixture of permanganate was determined by adding potassium iodide, titrating, adding ethyl alcohol, filtering off the manganese, and then titrating the chromium iodometrically (*83*). With acetylacetone manganese ions form a stable complex which has no action on potassium iodide, while under the same conditions tetravalent manganese chloride loses chlorine with acetylacetone which liberates iodine from potassium iodide (*79*).

Mercury. Traces of mercury are distilled and determined by a dithizone titration (*148*). Mercuric ion reacts with acetone to give hydrogen ion which can be titrated with alkalies (*62*). A method similar to that of Volhard for silver is applicable to mixtures of mercurous and mercuric ion (*36, 38*).

Nitrogen. Nitrite is reduced with zinc powder and sodium carbonate. The ammonium formed is titrated in the usual manner (*106*). A critical survey of the methods for nitrates has resulted in one in which the nitrate is reacted with permanganate and iodide, and the liberated iodine is titrated (*33*). By absorbing in sulfuric acid, nitric oxide and nitrogen tetroxide may be determined by analyzing for total nitrogen with a nitrometer and for nitrosyl nitrogen by permanganate titration (*242*). A review of micro Kjeldahl methods has been made (*29*) and nickel sulfate is proposed as an absorbent. Aluminum nitride in steel is determined by reacting with an ester-halogen solution, removing the aluminum nitride by filtration and then using the Kjeldahl method (*12*).

Oxygen. Ozone in high concentration has been absorbed in potassium iodide and the iodine liberated is titrated with thiosulfate (*31*). For dissolved oxygen, the sample is added to standard chromous chloride and excess chromous ion determined by adding potassium iodate and titrating with chromous ion; the apparatus is described (*212*). For determining oxygen in metal oxides, the oxide is reacted with sulfur and the liberated sulfur dioxide is determined iodometrically (*58*).

Palladium. Organic compounds, especially furfural dioxime, were used to precipitate palladium, which was then treated with vanadyl sulfate and the excess titrated with ferrous sulfate (*215*). In another method, after precipitating as chloropalladate, the precipitate is dissolved in standard ferrous sulfate and excess ferrous sulfate titrated (*214*).

Phosphorus. After surveying methods for determining phosphate, a method was developed in which phosphate is precipitated as quinoline phosphomolybdate and the precipitate is titrated with standard hydrochloric acid (*246*). For iron ores, modifications of the ammonium phosphomolybdate method have been used (*117, 118*).

Potassium. Modifications of the cobalt nitrite method include titration with sulfuric acid (*88*) and with dichromate (*108*).

Selenium. A control method for metallic copper and pyritic material consists of distilling selenium as tetrabromide and after adding potassium cobalticyanide and potassium iodide, titrating with thiosulfate (*140*). A similar procedure precipitates selenium before the iodometric titration (*158*). By using pyrophosphoric acid as a complexing agent and iodine monochloride as a catalyst, a rapid method for selenium in the presence of tellurium has been developed (*219*).

Silicon. A conductometric titration using lead nitrate has been proposed (*14*). In modifications of the fluorosilicate method, standard hydrochloric acid is added to the silica and potassium fluoride and the excess acid is titrated with standard potassium hydroxide (*192, 198*). Fluorosilicic acid has been determined by a method which is essentially that of Scott and Furman (*226*).

Silver. Silver is determined in the presence of lead and copper by adding it to a blue starch-iodine solution in the presence of potassium iodide, causing the indicator to fade. Calibration of the method under similar conditions is required (*39*).

Rapid determinations have been made by the addition of a measured volume of hydrochloric acid and titration of the excess with standard alkali (*54*).

Ultramicro quantities were determined by two methods (*228*)—titration with 0.005 to 0.01 *N* ammonium thiocyanate using ferric ammonium sulfate as indicator and titration with the silver salt solution of an iodide solution with iodo-starch indicator.

Sodium. Alloys of sodium and aluminum are separated by vacuum distillation and the sodium is precipitated with zinc uranyl acetate. The uranium is then titrated using titanous chloride (*135*).

Another indirect application of the zinc uranyl acetate method employs the lead reductor to reduce the uranium (*139*). In the presence of antimony, the antimony is distilled as chloride and the sodium chloride left behind is titrated with silver nitrate (*128*). Sodium oxide in metallic sodium is determined by removing metallic sodium with mercury and titrating the oxide with hydrochloric acid (*171*).

Strontium. For a rapid determination, precipitation with standard sulfuric followed by titration of excess acid has been used (*54*).

Sulfur. A photometric titration using lead nitrate and alcohol has been proposed for sulfate (*223*). In another method for sulfate, barium iodate is used, followed by iodometric titration (*204*). Sulfate can also be determined by precipitating sulfate with barium, the excess barium then being titrated with Versene (*152*). By using stannous chloride, sulfate can be reduced to hydrogen sulfide, which can then be determined iodometrically (*178*). In a rather complicated procedure involving fuming in hydrogen, sulfur is converted to hydrogen sulfide which is converted to polysulfide and titrated with hypochlorite (*124*).

Sulfur is determined by boiling with standard sodium hydroxide and titrating the excess alkali (*77*). It has been stated that for accurate results the usual iodometric method for determining sulfur in steel is not accurate. Alkaline hypochlorite is stated to have advantages (*125*). Polysulfides are dissolved in excess standard potassium iodide containing carbon disulfide. After adding thiosulfate the excess is determined with standard iodine (*61*). Complete procedures for commercial alkali polysulfides (*90*) and sulfate, sulfide, and polysulfides have been given (*191*).

Tellurium. The tellurium in metallic copper is separated with hypophosphite, dissolved with bromine, and, after adding potassium cobalticyanide and sodium hypophosphite, titrated with iodine (*158*).

Thallium. For small amounts, a dithizone separation followed by iodometric titration has been used in ores and flue dust (*201*), while for zinc-cadmium solutions an oxidation with bromine followed by iodometric titration has been used (*121*).

Thorium. A review (*59*) of the general analytical chemistry of thorium contains some volumetric methods but since thorium has only one valence, indirect methods are used. A modification of the oxalate precipitation–permanganate method has been reported (*143*). A direct titration with sodium oxalate using the high-frequency titrimeter can be used (*24*).

Tin. The lead reduction–iodometric procedure has been used for bearing metals (*181*), bronzes (*159, 161*), pig tin (*116*), and ores (*52*). For cable sheathing alloys, after determining antimony, reduction with sodium hypophosphite, followed by iodometric titration, has been used (*19*). In the usual method using nickel as reductant, it is shown that some tin is coprecipitated with the antimony (*104*).

Titanium. Titanium(III) has been oxidized with vanadium pentoxide during solution and the excess vanadium is titrated with ferrous ion (*136*). If acetic acid and ammonium sulfate are used, it is stated that titanium(III) can be titrated without interference of oxygen of the air (*218*). Titanium is reduced with metallic iron and titrated with ferric ion (*17, 18*) in titanium-rich residues and modification of the thiosulfate method for ferrotitanium is given (*53*).

Uranium. The interest in this element continues as is shown by the review (*187*) and books (*40, 186*) recently published. The use of the lead (*49*), zinc spiral (*138*), and bismuth amalgam (*130*) reductors has been advocated. For ores, a mercury cathode-cupferron modification has been proposed (*176*). Small amounts of uranium have been determined using chromous chloride as a reducing agent (*50*); sodium vanadate has been proposed as an oxidant (*155*).

Vanadium. Modifications of the ferrous sulfate method have included a dead-stop end point (*80*), a photometric end point (*87*), and a method for steel (*110*). For the separate determination of vanadium(IV) and vanadium(V), bicarbonate and acetone are used to precipitate, followed by reduction of vanadium (V) with ferrous sulfate and total vanadium by the persulfate–ferrous sulfate method (*151*). In another method, vanadium (II), vanadium(III), and vanadyl(II) are titrated with permanganate, and vanadium(III) with permanganate using diphenylamine as indicator. The vanadium(II) is oxidized to vanadium(III) with silver(I) and then titrated (*153*).

Water. There has been considerable interest in the Karl Fischer method as shown by reviews (*114, 149, 150*). Applications have been made to water in air (*188*) and gaseous hydrogen chloride (*147*). Suggestions for standardization of reagents (*182*) and the use of sodium tartrate dihydrate as a standard (*156*), as well as improvements in measuring apparatus, have been made (*243*).

Zinc. Zinc is precipitated as oxalate using ethyl oxalate and the precipitate is dissolved and titrated with permanganate (*41*). A modification of the oxine-bromate method has been used for aluminum alloys (*211*). Conditions for using the ferrocyanide method have been given (*63*).

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Volumetric Analytical Methods for Organic Compounds

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THIS discussion is based primarily on reports that have become available from September 1950 to October 1951.

DETERMINATION OF ELEMENTS

HALOGENS

In a new variation on the Parr bomb fusion a nickel bomb (with 0.3% manganese) of 10 ml. capacity is used. Eight drops of ethylene glycol and the sample are placed in the bomb and covered with 3 to 11 grams of sodium peroxide. The bomb is closed and heated with a microburner for 10 to 20 seconds to ignite the mixture. After about 50 seconds of heating the bomb is quenched in water. One of the advantages claimed for this decomposition procedure lies in the fact that the bomb is not subjected to as severe service as in the usual sugar–sodium peroxide procedure because the ignition temperature of the sodium peroxide–ethylene glycol mixture is 58° (*161*). However, it seems that this low ignition temperature constitutes a safety hazard, and care should be exercised in using this method.

The following methods are used by Martin (*94*) for analyzing the decomposition products from the usual sodium peroxide Parr bomb fusion.

The residue from the fusion is dissolved, boiled to decompose sodium peroxide, and treated with sufficient nitric acid to bring the concentration of the final solution to 25% nitric acid. Chloride is determined by the usual methods after bromine and iodine are removed by passing air or nitrogen through the solution. Bromide is oxidized by sodium hypochlorite to bromate and the excess hypochlorite is removed by the addition of sodium formate. The bromate is then determined iodometrically. This method cannot be used in the presence of iodide. Iodide is oxidized by bromine water in neutral solution, and after the bromine is boiled off, the iodate is determined iodometrically.

In a combustion method a tube filled with quartz wool is used. The products of the decomposition are absorbed in a mixture of 3 ml. of Perhydrol and 7 ml. of water contained in a detachable spiral. The halide is determined argentometrically using dichlorofluorescein indicator (*46*).

The method of Freeman and McCullen (*40*) has been modified and subjected to collaborative study. The somewhat variable results indicate that further study is necessary before the procedure can be recommended (*142*).

Two methods for the determination of halogens in halogenated fluoresceins (*8, 67*) have been studied collaboratively with satisfactory results (*66*).

Organic bromine compounds may be decomposed by treatment with lead-free zinc and 10% sodium hydroxide solution, followed by oxidation of the organic residue with permanganate (*47*). An alternative is to decompose a 3- to 4-gram sample by adding it to melted potassium. The excess potassium is decomposed with methanol and the methanol is removed by distillation (*71*).

The analysis of fluorocarbons has been discussed in some detail. A combustion train is described which permits the determination of carbon, fluorine, and chlorine in a single sample if the sample contains no hydrogen (*85*). The determination of fluoride has been reviewed with particular attention paid to the titration of fluosilicic acid with thorium nitrate using sodium alizarin sulfonate as indicator.

Colorimetric indicators for the titration of fluoride with thorium salts have been rated in the following order of decreasing effectiveness: purpurin sulfonate, Alizarin Red S, Eriochromecyanin R, dicyanoquinizarin, and Chromazurol S. The best fluorometric indicators are morin and quercetin. Optimum conditions include an alcohol concentration of 50% and a pH range of 3 to 4 (*158*).

MERCURY

Mercury in organic molecules has been determined as follows (*61*).

A 3- to 5-mg. sample is placed in a Kjeldahl flask and 2 ml. of concentrated sulfuric acid containing 0.4 gram of potassium sulfate are added. The mixture is boiled gently for 20 to 25 minutes. The solution is cooled and 5 drops of 30% hydrogen peroxide are added. The solution is boiled 10 to 15 minutes, and the treatment with hydrogen peroxide is repeated. The solution is diluted with 15 ml. of water and the mercuric ion is titrated with ammonium thiocyanate by the Volhard method.

NITROGEN

Moelants has critically reviewed the combustion methods for the determination of nitrogen in organic compounds (*103*). A combustion tube filling similar to that of Friedrich (*41*) but without the lead dioxide is recommended.

In another apparatus a combustion tube containing no lead dioxide is used and nitrogen and hydrogen are determined simultaneously by putting a water absorption tube between the combustion tube and the azotometer. Carbon may be determined in separate combustion using the same tube (*162*).

Improvements for the Dumas method for nitrogen include an electric furnace for automatic burning and an improved Kipp generator for generating carbon dioxide free from air (*30*).

Ring nitrogen is not attacked in the Kjeldahl procedure if the compound is reduced by hydriodic acid and red phosphorus and then subjected to concentrated sulfuric acid, mercuric acetate, and potassium sulfate. The difference between the result obtained in this way and that obtained by the Dumas method is a measure of the ring nitrogen in the sample (*96*, *97*).

The kinetics of the Kjeldahl determination on aniline have been studied using selenium, copper, mercury, and copper-mercury catalysts and also without catalysts. In all cases the reaction was first order with respect to aniline. The various catalysts were effective by different mechanisms (*134*).

A systematic study of the effect of selenium oxychloride and potassium sulfate on the Kjeldahl determination of pyridine indicates that all the pyridine nitrogen is obtained by heating 0.15 gram of pyridine, 0.5 gram of selenium oxychloride, and 40 grams of potassium sulfate for 1 hour (*33*).

It appears that preliminary reducing treatment may not be necessary in the determination of nitrile-type nitrogen by the Kjeldahl method. In a wide variety of cases over 98% of the nitrogen was recovered when the reducing treatment was omitted (*151*).

Several other variations on the Kjeldahl procedure have been reported (*12*, *43*, *92*, *113*, *115*).

For the Dumas determination of nitrogen in compounds that are hard to burn completely it has been recommended that the sample be burned in a platinum boat with the help of copper oxide, in a stream of moist carbon dioxide and oxygen. The gas mixture is passed over heated copper at the front end of the combustion tube to remove the excess oxygen and the nitrogen is collected in an azotometer over potassium hydroxide solution as usual (*150*).

OXYGEN

Experiences during the past ten years in the use of the Unterzaucher method (*149*) have been reviewed (*150*).

A variety of thermal decomposition methods for the direct determination of oxygen in organic compounds has been discussed (*4*).

In a semimicroprocedure (*28*) the sample is pyrolyzed at 1050° to 1100° C. in a stream of oxygen-free nitrogen. The oxygen is converted into carbon monoxide by passing over carbon at the same temperature, and the carbon monoxide is oxidized by mercuric oxide to carbon dioxide, absorbed in barium hydroxide solution, and determined titrimetrically. The method requires about 1.5 hours. The relative accuracy is 2%.

SULFUR

In a procedure for sulfur the sample is burned in a stream of oxygen and the escaping gases are brought into contact with a stream of hydrogen. In the hydrogen-oxygen flame hydrogen sulfide and a very little free sulfur are formed and are absorbed in strong sodium hydroxide solution. The sulfide and polysulfide thus formed are titrated oxidimetrically with standard hypochlorite solution. Since the valence change of the free sulfur is from 0 to 6 and the hydrogen sulfide from 2 to +6, the results are usually a little low (*76*).

The use of the Zimmermann method (*165*) for determination of sulfur in sulfanilic acid, sulfanilamide, sulfathiazole, and sulfamerazine has been reported (*58*).

FUNCTIONAL GROUPS

ACETYL

The method described by Clark (*22*) has been modified for the determination of acetyl groups in pectin (*114*).

Acetates of hydroxyethylcellulose have been saponified with aqueous-alcoholic potassium hydroxide solution to give saponification equivalents which become slightly lower with longer saponification periods (*24*).

ACTIVE HYDROGEN

In a variation on the determination of active hydrogen, methyl magnesium iodide in ether is mixed with the sample in pyridine. The methane formed is forced into an azotometer by ether vapor. The ether vapor is absorbed in 50% aqueous alcohol in the azotometer (*147*).

In an elaborate lithium aluminum hydride method the sample is brought in contact with a solution of lithium aluminum hydride in *n*-propyl ether. The hydrogen formed is carried by nitrogen to a combustion tube containing cupric oxide at 1100° to 1120°, where it is converted to water. The water on contact with hot carbon is converted to carbon monoxide, which subsequently reacts with iodine pentoxide to liberate iodine. The iodine can then be determined by titration (*132*).

ACIDS

A large variety of organic compounds may be titrated as acids with 0.1 *N* sodium methoxide in benzene-methanol if the proper nonaqueous solvent is employed (*42*). Most carboxylic acids can be titrated in benzene-methanol solutions. Acid chlorides and anhydrides may be titrated as strong monobasic acids in benzene or benzene-methanol. Enols cannot be titrated sharply in benzene-methanol, but give good results in butylamine. Succinimide also behaves as a strong acid in butylamine. Nitromethane may be titrated in butylamine, but the results are low and erratic, perhaps because of partial decomposition. Butylamine serves as a suitable solvent for the titration of thiophenol and 2-mercaptobenzothiazole. Strychnine sulfate and β-bromoethylamine hydrobromide can be titrated in benzene-methanol. Hydroxylamine hydrochloride is insoluble in benzene-methanol, but may be titrated in pyridine. The end points are determined either potentiometrically or by use of thymol blue indicator.

A modification of the bromometric method of Maeder (*86*) for the determination of formic acid has been described (*117*).

In a vapor phase study, acetic acid is condensed in a sample tube, sealed off, broken under carbon dioxide–free water, and titrated with standard barium hydroxide solution to a phenol red end point (*146*).

Acetic acid arising from the alkaline cleavage of substituted acetylacetones has been determined in the presence of excess β-diketone by a titration procedure. The thymol blue indicator used does not give too sharp an end point (*111*).

Carboxyl end groups in polyaminocaproic acid have been determined by the following method.

A 100-mg. sample in 3 ml. of boiling β-phenylethyl alcohol is quickly diluted with 10 ml. of *n*-propyl alcohol–water azeotrope, and the indicator (120 mg. of phenolphthalein and 18 mg. of thymol blue in 1 liter of aqueous ethyl alcohol) is added. The solution is placed in a photometric colorimeter, stirred with nitrogen gas, and titrated with 0.01 *N* sodium hydroxide (*131*).

ALCOHOLS

The formylating reagent of Glichitch (*52*) has been used recently for the determination of primary, secondary, or tertiary alcohols (*128*). It is necessary to carry out control runs along with the samples to be analyzed. The method presumably is valuable for determining alcohols that are easily dehydrated.

The acetic anhydride–pyridine technique has been used to determine the equivalent weight (per hydroxyl) of hydroxyethylcellulose (*24*).

ALDEHYDES AND KETONES

Carbonyl compounds have been determined in the following way.

The sample is treated with excess 2,4-dinitrophenylhydrazine and hydrochloric acid. The excess reagent is then treated with a known amount of titanous chloride (12 moles of titanous chloride per mole of dinitrophenylhydrazine), and the excess titanous chloride is titrated with ferric alum to a thiocyanate end point (*133*).

The hydroxylamine hydrochloride method of Bryant and Smith (*17*) has been used for the analysis of the combined isobutyraldehyde and methyl ethyl ketone arising from the pinacol rearrangement of isomeric 2,3-butanediols (*3*).

In a kinetic study of the condensation of aniline and substituted anilines with formaldehyde in aqueous hydrochloric acid, use has been made of the sulfite method for estimation of the total amount of formaldehyde, methylene aniline ($C_6H_5N{=}CH_2$), and the cyclic trimer of methylene aniline (*110*).

Some previously described methods for furfural and pentosans (*108*, *109*) have been reinvestigated and found useful (*16*). Furfural is determined by adding an alcholic solution of hydroxylamine hydrochloride and titrating the hydrochloric acid liberated with 1 *N* sodium hydroxide solution to a bromophenol blue end point. As pentosans and pentoses yield furfuraldehyde when suitably heated with hydrochloric acid, the method can be applied also to their determination.

Vanillin has been determined by oxidizing the sample in 1 *N* sodium hydroxide solution with hydrogen peroxide and titrating the excess alkali with 1 *N* hydrochloric acid to a phenolphthalein end point. A blank is necessary (*138*).

Acetone has been determined in the presence of di-*tert*-butyl peroxide by the method of Maltby and Primavesi (*88*). Their procedure has been modified by using only a 20 to 30% excess of hydroxylamine hydrochloride and by using a pH meter rather than an indicator for the end point (*32*).

In order to follow the concentration of acetylacetone during basic ethanolysis, the following procedure has been used.

The sample is added to 0.1 *N* acid and excess bromine water is added. After 4 minutes phenol is added, followed by potassium iodide. After 5 to 10 minutes the reaction mixture is titrated with 0.1 *N* thiosulfate solution (*112*). Theoretically, 4 moles of thiosulfate should correspond to 1 mole of ketone, but in actual practice the value was 3.77 (94%). This could be increased to 3.87 (97%) by increasing the contact time of the potassium iodide solution.

AMINES

In a study of the aminolysis of esters, a variety of amines were determined in the presence of esters by titration with aqueous 0.05 to 0.1 *N* hydrochloric acid to methyl red–methylene blue indicator. The following amines were used: *n*-butylamine, piperidine, morpholine, isobutylamine, methyl-*n*-butylamine, and methylisobutylamine (*10*).

Under proper conditions the action of nitrous acid on 1,4-diphenylenediamine to diazotize one amino group is quantitative and the reaction has been used for the determination of 1,4-diphenylenediamine (*139*).

The previously described procedure of Watanabe and Ishinose (*155*) for the determination of aromatic primary amines has been revised so that solid samples may be analyzed, and small amounts of reagents may be used (*156*).

A study has been made of the amount of nitrogen evolved when various heterocyclic amines are diazotized (*145*).

Pyridine carboxylic acids dissolved in acetic acid have been titrated with 0.1 *N* perchloric acid in acetic acid using a methyl violet indicator. An end-point blank is necessary. The mean error is ±1% (*70*).

Methods have been described for analyzing the basic products formed in the reaction between aqueous ammonium salts and formaldehyde (*9*).

The titration of weak bases with perchloric acid in acetic acid has been discussed (*89*, *135*). Potassium acid phthalate is recommended as a primary standard (*135*).

AZO GROUPS

1,1′-Azobis(1-arylalkanes) have been shown to decompose quantitatively in ethylbenzene to yield nitrogen gas, which is swept by a current of carbon dioxide into an azotometer containing 40% potassium hydroxide and the volume is measured (*23*).

DIAZONIUM GROUPS

By measuring the amount of nitrogen evolved in the following reaction

$$ArN_2Cl + I^- \longrightarrow ArI + N_2 + Cl^-$$

aromatic diazonium salts have been determined. Naphthols may also be determined by coupling with an excess of diazonium salt, followed by determination of the excess by the above reaction. The methods are not very exact, but are said to be suitable for plant control work and comparison measurements (*45*).

ESTER GROUPS

The determination of the saponification number of resins and other difficultly saponifiable esters is facilitated by use of a diethylene glycol solution of potassium hydroxide containing about 8% phenetole. The phenetole increases the solvent power of the reagent and excludes atmospheric oxygen from the reaction mixture by providing a blanket of vapor over it (*136*).

A solution of potassium hydroxide in a 1 to 1 mixture of Cellosolve and xylene is described as an ideal reagent for determining saponification equivalents (*54*).

HYDROXAMIC ACIDS

Long-chain hydroxamic acids have been determined by hydrolysis with a known amount of hydrochloric acid in aqueous ethyl alcohol. The excess hydrochloric acid is titrated with standard sodium hydroxide. The results obtained are slightly low. An alternative procedure involves titration of the hydroxylamine hydrochloride formed. This method gives results which are slightly high. The hydroxylamine hydrochloride cannot be titrated in the presence of fatty acids containing ten or less carbon atoms (*125*).

OXIRANE GROUP

Ethylene oxide reacts quantitatively with hydrochloric acid containing magnesium chloride or calcium chloride and the excess hydrochloric acid may be determined by titration

with standard base to a methyl red end point. Pure magnesium chloride is essential. Calcium chloride gives a constant factor of 1.01 (*101*). This method is similar to the one of Lubatti (*84*) which has been used for the determination of ethylene oxide in mixtures containing acetaldehyde, formaldehyde, and acetic acid (*104*).

In a different procedure (*34*) a 1-ml. glass bulb containing 0.1 to 0.2 gram of ethylene oxide is broken under the surface of a 1% solution of periodic acid in 4 *N* perchloric acid. After 45 minutes, the excess periodic acid is determined by a standard method (*63*).

PEROXIDES

Again as last year a number of investigators have used iodometric methods for the analysis of various peroxides. In general, either acetic acid or acetone has been used as a solvent. The decomposition of the peroxide by the iodide is carried out in the warmed solution in an atmosphere of carbon dioxide usually supplied by dry ice. Titration is with standard thiosulfate. The use of acetone as a solvent is not complicated by iodination under the conditions of the reaction. Such methods have been described for acetyl peroxide (*126*), lauroyl peroxide (*20*), substituted benzoyl peroxides (*13*, *143*), *tert*-butyl perbenzoate (*14*), peroxides formed during the autoxidation of benzaldehydes (*154*), and benzoyl peroxide in the presence of iodine, which must be removed by titration with thiosulfate before the determination is carried out (*56*).

SULFONAMIDES

Sulfonamides have been determined by titration with bromine in acetic acid in the presence of sodium acetate (*31*). A similar approach has been the titration with sodium hypochlorite. The sulfonamide solution is kept basic so that the reaction observed is:

$$RSO_2NH_2 + NaOCl \longrightarrow RSO_2NClNa + H_2O$$

The titration is carried out in the following fashion.

A weighed amount of the sulfonamide is dissolved in warm sodium hydroxide solution. The solution is cooled to room temperature, diluted with water to 100 ml., and placed in a Dewar flask. The solution is stirred mechanically for 15 minutes. The standard sodium hypochlorite solution is then added slowly in 2-ml. portions at first but in smaller portions as the reaction progresses. After each addition the temperature, measured by a Beckman thermometer, is recorded as soon as it becomes constant, usually in about 30 seconds. A plot of volume of sodium hypochlorite solution added against temperature yields a line that is nearly straight. At the equivalence point a change in slope is observed. Values obtained are accurate to about 1% (*137*).

In a general discussion of methods for sulfonamide analysis the volumetric methods are considered to be more accurate than the colorimetric methods. The nitrite titration to the starch–potassium iodide end point is believed the most specific. Other indicators are also discussed (*2*).

UNSATURATION

Analyses for individual olefins or general determinations of unsaturation—e.g., the iodine number—have been carried out most frequently by bromine addition. Ethylene gas has been determined by absorption in an excess of a solution of bromine in acetic acid followed by an iodometric titration of the excess bromine (*100*). Styrene and α-methylstyrene have been determined in nitrobenzene–carbon tetrachloride solution in the presence of their polymers, stannic chloride, and amines by direct titration with bromine in carbon tetrachloride (*49*, *50*). Dienes have been similarly determined in acetic acid solutions containing potassium acetate by direct titration with bromine in acetic acid (*80*).

The method of Kaufmann (*72*), which involves reaction with bromine in methanol followed by titration of the excess bromine with arsenite solution, has been found more accurate than other methods for the determination of the iodine numbers of several α,β unsaturated acids (*129*). Similarly the iodine numbers of several phenols, cholesterol, limonene, naphthalene, oleic acid, and various essential oils have been determined in acetic acid solution (*148*).

Kaufmann's reagent (*73*), bromine in methanol saturated with sodium bromide, has been applied to the measurement of unsaturation in motor fuels (*159*).

The objections of Joshel, Hall, and Palkin (*68*) to the use of halogen in the determination of unsaturation in terpenes because of the ease of substitution are reported to have been overcome. The method is a modification of that of Francis (*39*) and is carried out as follows (*35*).

A 1-ml. sample is placed in a glass-stoppered Erlenmeyer flask. A volume of 10% sulfuric acid about 1.5 times as large as the volume of bromide-bromate solution required (determined by a trial run) is then added. The 0.5 *N* bromide-bromate solution (14 grams of potassium bromate and 50 grams of potassium bromide per liter) is added in 5-ml. portions at first and in 0.5-ml. portions toward the end of the determination when the reaction slows down. After each addition the flask is shaken vigorously until the color disappears. The reaction is considered to be complete when the color persists for more than 30 seconds. The addition of 5 ml. of 10% potassium iodide solution followed by titration with 0.2 *N* sodium thiosulfate completes the determination.

The method of Kemp and Mueller (*75*) for the determination of unsaturation by the addition of iodine chloride has been applied to the analysis of polyisoprene, rubber, and gutta-percha. With chlorinated polymers the method must be modified in order to allow longer times for addition of the iodine chloride (*78*).

The volume of hydrogen taken up over palladium on charcoal has been used for the determination of the iodine number of isomerized linoleic acid and its ester (*107*). A similar determination capable of measuring the hydrogen uptake of less than 1 mg. of sample has also been described (*98*).

The iodine equivalents of the diene numbers of dienes have been determined by a modification of the method of Kaufmann and Baltes (*74*) in which the diene reacts with excess maleic anhydride in the presence of iodine, which catalyzes cis-trans isomerization. The product is separated, and the excess anhydride is determined by titration (*99*).

Terminal triple bonds have been determined by the reaction in neutral aqueous or alcoholic solution with silver benzoate. After filtration, titration of the acid gives a measure of the number of terminal triple bonds (*93*).

MISCELLANEOUS METHODS

LITHIUM DERIVATIVES

The concentrations of methyl lithium and phenyl lithium have been determined in *n*-butyl ether containing ethyl ether and *n*- or *tert*-butyl chloride by titration with 0.1 *N* hydrochloric acid to the lacmoid end point. The determination was checked in the case of methyl lithium by the Zerewitinoff-type determination of the methane formed (*25*, *26*).

MERCURY DERIVATIVES

Nonhalogen mercurials when treated with sodium chloride give compounds of the type RHgCl. The excess sodium chloride is determined by the Volhard method. With a compound of the type RHgR′ a reaction with acetic acid is carried out to give the acetoxymercuri compound, which is then treated with sodium chloride as above. Similarly, a halomercuri compound is first treated with moist silver oxide in alcohol to give the corresponding hydroxymercuri compound, which is then treated with sodium chloride (*124*).

MIXTURES

Mixtures of hydrocarbons containing saturated, unsaturated, and aromatic hydrocarbons have been analyzed by selectively dissolving the unsaturated hydrocarbons in one reagent (5 grams of boric acid in 100 ml. of concentrated sulfuric acid) and the unsaturated and aromatic hydrocarbons in a second reagent (30 grams of phosphorus pentoxide in 100 ml. of concentrated sulfuric acid). The method is effective if no more than a maximum of 30% of the mixture is absorbed in a reagent. For cases in which more is absorbed, dilution with chloroform is suggested (*152*).

Similar selective absorption has been used to determine the composition of mixtures of carbon disulfide, thiophene, and carbonyl sulfide. The thiophene is absorbed by 93% sulfuric acid, the carbon disulfide by 93% sulfuric acid containing spindle oil, and the carbonyl sulfide is obtained by difference (*121*).

Mixtures of amines have been titrated with standard hydrochloric acid to obtain the total basicity of the mixture. A similar titration after acetylation with acetic anhydride gives a direct measure of the amount of tertiary amines. Titration of the mixture after reaction with salicylaldehyde measures the amounts of secondary and tertiary amines combined. The individual amounts of primary and secondary amines are then determined by difference (*140*).

The Grignard reagent in mixtures of *n*-hexyl magnesium bromide and benzyl chloride has been determined by the method of Gilman (*51*), except that no heating is used.

After the addition of cold water, standard acid is added, and the mixture is allowed to stand 1.5 hours. The excess acid is titrated with standard base. After the titration 50 ml. of 0.2 *N* sodium hydroxide are added, and the volume is made up to approximately 150 ml. After the addition of 60 ml. of 95% ethyl alcohol the solution is approximately 0.045 *N* sodium hydroxide in 27% alcohol. The mixture is boiled 30 minutes under reflux, and the excess alkali is titrated to give a measure of the amount of benzyl chloride present. A blank run is carried out. Results accurate to ±2% are obtained (*130*).

Methanol in mixtures of methanol and ethyl alcohol has been determined in the following manner (*144*).

A 3-ml. sample is diluted to 100 ml. with water. To a two-compartment flask connected to a gas buret, 4.0 ml. of the diluted sample are added, and 1.5 grams of potassium chromate are added to the same compartment. To the other compartment are added 6 ml. of 18 *N* sulfuric acid. The system is closed and the solutions are mixed. The volume of carbon dioxide evolved is measured. A correction is necessary for carbon dioxide evolved by ethyl alcohol under the reaction conditions.

Mixtures of alcohols and amines obtained during the course of alkylation of amines by alcohols have been completely acetylated. Saponification under suitable conditions gives negligible hydrolysis of the amides, so that the saponification equivalent is a measure of the alcohol content (*141*).

A modified reagent containing cupric ion which oxidizes fructose selectively in the presence of glucose has been described. The cuprous oxide formed is dissolved in standard ferrous sulfate solution, and the excess ferrous sulfate is titrated with potassium permanganate solution. The combined fructose and glucose are oxidized by one of the standard reagents, and the amount of cuprous oxide formed is measured as above (*11*).

Mixtures of pinene and camphor have been treated with acetic acid containing sulfuric acid, formic acid, or formic acid containing acetic anhydride. In each case, camphor reacts to a greater extent than pinene. The excess reagent is titrated. A plot of the amount of reagent used *vs.* composition of known mixtures is necessary for each reagent (*37*).

Mixtures of ε-aminocaproic acid hydrochloride and hexamethylenediamine dihydrochloride from the hydrolysis of certain types of nylon polymers have been titrated directly with 0.1 *N* sodium hydroxide to the phenolphthalein end point to give a direct measure of the ε-aminocaproic acid hydrochloride which acts as a monobasic acid. Treatment of the mixture of hydrochlorides in aqueous solution with Amberlite IRA-400 ion exchange resin gives hexamethylenediamine in solution, which is determined by titration with 0.1 *N* hydrochloric acid to methyl orange (*57*).

Mixtures of benzoic acid, trityl chloride, trityl benzoate, and benzoyl peroxide in benzene when diluted with 2 volumes of ethyl alcohol and titrated with standard aqueous base give a measure of the benzoic acid plus the trityl chloride. A sample treated similarly and analyzed for chloride ion by a Volhard titration measures the trityl chloride present. A third sample diluted with ethyl alcohol containing 1 or 2 ml. of standard 0.1 *N* hydrochloric acid is heated at 54° for 20 to 30 minutes. Titration with sodium hydroxide gives the total analysis for benzoic acid, trityl chloride, and trityl benzoate. Under these conditions benzoyl peroxide yields very little acid. Analytical values for individual components are obtained by difference (*55*).

Determination of the components of commercial dimethyl sulfate has been carried out as follows (*69*).

A 1-gram sample of the mixture in 20 ml. of ethyl alcohol or methanol is titrated directly with standard 0.5 *N* sodium methoxide in methanol to bromocresol green. The total acidity resulting from methylsulfuric acid and sulfuric acid is obtained in this way. A 0.5- to 0.8-gram sample is treated with 25 ml. of cold aqueous 0.5 *N* sodium hydroxide for 1.5 hours. Titration of the excess sodium hydroxide with acid to bromocresol green gives a measure of the methylsulfuric acid, the sulfuric acid, and the dimethyl sulfate which is hydrolyzed to methyl sulfuric acid. A 20- to 25-mg. sample with 1 gram of potassium iodide in 2 ml. of water is allowed to react for half an hour at room temperature and then for half an hour at 50° C. The methyl iodide formed is determined by the usual Zeisel technique. Only the dimethyl sulfate reacts under these conditions.

SILICON DERIVATIVES

Compounds of the type $RSiI_3$, R_2SiI_2, and R_3SiI have been analyzed for iodine by the following procedure (*5*, *6*). A very thin-walled soft-glass capsule containing the sample is placed in the neck of a special round-bottomed flask containing double the theoretical amounts of sodium hydroxide and ethyl alcohol. The flask is stoppered and shaken until the capsule is shattered. In this way hydrogen iodide reacts with the base before ethyl iodide can be formed, and the excess alkali can be determined by titration.

SUGARS AND DERIVATIVES

Sugar in fruit juices, liquors, brandies, etc., has been determined by a method involving the titration of a standard potassium ferricyanide solution with the sugar solution containing zinc sulfate. The end point is a complete decolorization of the solution because the potassium ferrocyanide formed during the oxidation of the sugar is precipitated as $K_2Zn_3[Fe(CN)_6]_2$.

A 40-ml. sample of the standard 1% potassium ferricyanide solution is placed in a flask and 20 ml. of 2.5 *N* sodium hydroxide are added. The solution is brought to a boil and is then titrated with the sugar solution to which zinc sulfate has been added. The quantity of zinc sulfate varies from 3.4 grams per 100 ml. containing 0.1 gram of sugar to 20 grams per 100 ml. containing 0.5 gram of sugar. The potassium ferricyanide is standardized against refined sugar made up in concentration approximately equal to the concentrations of the unknown solutions. For very dilute sugar solutions a more dilute potassium ferricyanide solution should be used (*18*).

Phenyl β-D-glucopyranosyl sulfones have been analyzed by quantitative cleavage with sodium periodate.

A 0.17-gram sample in 5.00 ml. of 0.5 *N* sodium periodate is diluted to 20 ml. with water and allowed to stand at room temperature overnight. The reaction mixture is extracted continuously for 8 hours with ethyl acetate. The aqueous layer is transferred quantitatively and treated with excess sodium bicarbonate, diluted with 5 ml. of 0.05 *N* sodium arsenite and 1 ml. of 20% potassium iodide, and titrated with 0.05 *N* iodine solution after 10 minutes. In another determination the solution is not extracted with ethyl acetate nor neutralized, but is titrated with standard base to determine the amount of formic acid formed (*15*).

Aldoses may be determined by a quantitative application of the Kiliani reaction (*38*). At pH 8.5 and 39° hydrocyanic acid adds quantitatively to aldoses. The resulting cyanohydrin is hydrolyzed and the ammonia formed is determined by titration.

WATER

There have been several general discussions and reviews on the the use of the Karl Fischer reagent for the determination of water in organic compounds and mixtures (*59, 65, 102*). The preparation and standardization of the reagent have been discussed, and an alternative method of standardization which uses reagent grade methanol rather than anhydrous methanol has been suggested (*122*).

Sodium tartrate dihydrate has also been recommended as a primary standard for the Karl Fischer reagent (*106*).

Specifically the reagent has been used for the determination of water in preparations of xanthates and dithiocarbamates (*83*). Water formed as a product of the oxidation of methyl radicals has been determined by distillation from the reaction vessel into a known amount of Karl Fischer reagent held in a liquid nitrogen trap. A blank is run on the reagent in exactly the same way (*120*).

The amount of water formed during the Knoevenagel condensation has been followed by the volume collected in a phase separator after distillation with benzene or toluene (*119*). The volumetric determination of water by xylene distillation has been modified by the suspension of the sample by means of a wire basket in the vapor space above the xylene. Several samples can be analyzed on one charge of xylene. The method is reported to be especially useful for routine analyses of foods (*27*).

Water formed in the pyrolysis of phenyl phthalate has been determined by titration with toluene to an arbitrary cloud point (*164*).

A 10-ml. sample of the reaction mixture (a Carbitol solution) is diluted with 10 ml. of Carbitol. Titration with toluene gives an arbitrary, but reproducible, cloud point. A blank is run on 20 ml. of Carbitol. An experimentally determined plot of amount of water *vs.* volume of toluene shows a linear relationship for 10-ml. samples containing from 10 to 200 mg. of water.

UNCLASSIFIED

Acidimetric, bromometric, and iodometric methods for the determination of *p*-aminobenzoic acid have been described (*82*).

The method of Jermstad and Oestby (*64*) for caffeine has been modified by substituting potassium bromate and potassium iodide in acid solution for the iodine solution (*19*).

The following procedure has been used for the determination of anethole. A 5-gram sample is mixed with 10 ml. of a 20% solution of mercuric acetate and refluxed gently for 4 to 5 hours. The mixture is cooled, treated with 20 ml. of 10% potassium chloride and 25 ml. of 0.1 *N* iodine, and then back-titrated with sodium dithionites. Interference is caused by alcohols, ethylenes, and aldehydes, but methanol does not interfere (*21*).

The carbon dioxide resulting from lead tetraacetate cleavage of sugars in acetic acid is separated from most of the acetic acid by a water trap and then collected in a trap containing sodium hydroxide. Since some acetic acid is still present, barium chloride is added to the trap and the excess sodium hydroxide is titrated to a phenolphthalein end point. The barium carbonate precipitate is then titrated to a methyl orange end point (*1*).

To measure the reaction of diazoketones with acetic acid

$$RC(=O)\text{—}CHN_2 + CH_3CO_2H \longrightarrow RC(=O)CH_2OC(=O)CH_3 + N_2$$

the nitrogen evolved is collected in a gas buret over water saturated with nitrogen (*79*).

Cationic surface active compounds (such as 2-heptadecylglyoxalidine) which are used as fungicides on fruits have been determined by titration with a standard solution of an anionic surface active agent (dioctyl sodium sulfosuccinate) in a chloroform-water mixture using methylene blue indicator (*60*). At the start of the titration the indicator is in the water layer, but as the equivalence point is reached it forms a chloroform-soluble complex with the anionic reagent. The color intensities of both layers match at the end point.

It is reported that when crude DDT is treated with 0.5 potassium hydroxide for 60 minutes at 1° to 5° only the pure (*p,p'*- isomer) DDT is hydrolyzed, and its percentage in the crude material may then be determined by back-titration (*116*).

Chlorine in DDT can be eliminated in three stages, so that the amount of chlorine eliminated corresponds to either one, three, or five atoms of chlorine per molecule of DDT. To remove one atom of chlorine the sample is heated for 30 minutes at 250° with a small amount of ferric oxide and a measured excess of standard sodium hydroxide solution while air is passed through the apparatus. Saponification of DDT with potassium hydroxide in ethylene glycol liberates three of the five atoms of chlorine in the DDT molecule. To prove the presence of DDT in the sample, *p,p'*-dichlorodiphenylacetic acid may be isolated from the saponification reaction. All of the five atoms of chlorine may be determined by any of the usual methods for total chlorine (*157*).

Mixtures of the α-, β-, γ-, and δ-isomers of hexachlorocyclohexane may be analyzed by hydrolyzing the sample in four different ways (*127*). In each procedure the various isomers are hydrolyzed to different extents and from the combined data the percentages of the various isomers may be calculated. When 0.4 gram of sample is hydrolyzed with 0.4 *N* sodium hydroxide in methanol for 20 minutes at 100° all the isomers are converted to trichlorobenzene and labile chlorine is removed completely. When the above procedure is carried out for 20 minutes at 30° all but the β- isomer react. When treated with 0.0125 *N* sodium hydroxide in methanol for 15 minutes 63% of the α- and δ-isomers and 35% of the γ- isomer yield hydrogen chloride. In repeating this latter treatment for 30 minutes instead of 15, 80% of the α- and δ- isomers reacts and 51% of γ- isomer reacts. The amount of hydrogen chloride liberated under each of the above conditions is determined by titration with 0.02 *N* mercuric sulfate in the presence of diphenylcarbazone.

Phenolphthalein can be determined by oxidation with excess potassium bromate, followed by measurement of the excess.

A 0.1-gram sample is dissolved in 15 ml. of 0.1 *N* sodium hydroxide solution and treated with 8 to 10 ml. of 0.5 *N* potassium bromate, 5 ml. of 10% potassium bromide, and, with shaking, 25 ml. of an acid mixture (20 ml. of 80% acetic acid and 5 ml. of concentrated hydrochloric acid). The shaking is continued for 1 minute and then 1 gram of potassium iodide is added and the liberated iodine is titrated with 0.1 *N* sodium thiosulfate. Each milliliter of 0.1 *N* potassium bromide is equivalent to 0.003977 gram of phenolphthalein. A blank should be run (*118*).

Bis(diethylthiocarbamyl)disulfide has been determined in the following way.

The sample (0.4 to 0.5 gram) is dissolved in carbon tetrachloride and to 3 to 4 ml. of this solution are added 5 ml. of carbon tetrachloride, 10 ml. of water, and 10 ml. of concentrated hydrochloric acid. The mixture is titrated with 0.1 *N* bromate-bromide solution. A blank determination is necessary. By substituting chloroform for carbon tetrachloride the method can also be used for bis(dimethylthiocarbamyl)disulfide (*36*).

The ion exchange resins, Amberlite IR-120 (H form) and IR-4B (OH form), are used to remove all electrolytes of low molecular weight from aqueous solutions of high molecular weight pectins and pectates. By suitable analyses and calculations, carboxyl, ester, methoxyl, and acetyl groups may be determined on the resultant solutions (*7*).

Some previously described methods (*48, 87*) have been used recently for starch acetates, propionates, butyrates, caproates, palmitates, and benzoates (*160*).

The following procedure has been used for the determination of sodium alginate (*44*).

Twenty-five milliliters of a solution containing 3 to 15 mg. of lium alginate are mixed with 40 ml. of 0.01 N ceric sulfate,) mg. of silver sulfate, and 5 grams of potassium sulfate. The xture is boiled gently for 2 minutes, diluted to 100 ml. with cold er, and filtered through a dry filter. A 50-ml. aliquot of the ate is titrated with a standard ferrous ion solution to a ferroin end point. One milliliter of 0.1 N solution is equivalent to 1.2 mg. of sodium alginate.

Terminal bromodinitromethyl groups, $—CBr(NO_2)_2$, can be determined by a halogen analysis. Treatment of compounds containing these groups with an alkaline reagent was unsatisfactory because the color of the resultant solutions obscured the end point for the subsequent silver nitrate titration. However, these groups can be determined satisfactorily by treating the sample with potassium iodide and titrating the iodine liberated with standard thiosulfate (*77*).

In some kinetics studies alkyl sulfuric acid and unchanged sulfuric acid were determined by titration with standard base (*29*).

The concentration of acetate ion in acetic acid has been followed by titration with a standard solution of *p*-toluenesulfonic acid in glacial acetic acid, or, better, by adding a slight excess of the standard acid solution and back-titrating with sodium acetate in acetic acid (*163*).

A rapid method for determining aconitic acid in molasses, solutions from fermentations, and crude aconitates utilizes oxidation with standard potassium permanganate solution (*81*). The titration is carried out in a slight excess of sulfuric acid and at boiling temperature. The amount of oxygen consumed depends upon the concentration of the permanganate used, and not upon the concentration of aconitic acid. The amount varies from 15 oxygen atoms per molecule of aconitic acid with 0.05 to 0.1 N permanganate to the theoretical 9 oxygen atoms per molecule of aconitic acid with 1 N permanganate. As carried out the procedure is empirical, and the permanganate solution is standardized against a pure sample of aconitic acid. The results compare favorably with those obtained by the more complex decarboxylation procedure (*123*). The permanganate titration procedure can also be used for itaconic acid, but is not satisfactory when the samples are impure.

Iodometric equivalent weights of diaryl selenoxide–mercuric halide complexes have been obtained by dissolving a sample in warm methanol, adding an excess of acidified potassium iodide solution, and titrating the released triiodide ion with standard thiosulfate (*53*).

Betaine may be precipitated quantitatively as the reineckate and washed free of inorganic acid with ether. The precipitate is then dissolved in aqueous acetone and the reineckate ion is removed by addition of excess silver nitrate. The resulting solution of betaine nitrate is then titrated with sodium hydroxide, using methyl red indicator (*153*).

The acid number of oils and resins has been determined in aqueous medium by a process which involves using an emulsified sample (*105*).

A modification of previously described procedures (*90, 91, 95*) using mercuric acetate for the determination of unsaturation has been applied to the determination of rotenone (*62*).

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Characterization of Organic Compounds

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THE accepted requirements for full characterization of an organic compound include establishment of purity of sample, determination, of physical properties, determination of elementary composition, functional groups, and empirical formula, and elucidation of structural formula and spatial relationships. It is evident that identification of a known molecule will involve less extensive investigation than full characterization of a complex new compound. The characterization of simple or complex compounds may be accomplished by any of a wide variety of techniques and methods, some of which are more effective than others. The choice of criteria and procedural steps is often dependent on availability of special equipment. Infrared absorption spectra and x-ray diffraction patterns alone, for example, are sufficient to identify many known substances; identification carried out by chemical methods, while sometimes more time-consuming, is equally effective.

A consequence of the recent increase in number and scope of chemical studies of naturally occurring organic substances is seen in the widely held view that thorough training in principles of characterization is of fundamental importance for students majoring in organic chemistry. A comprehensive treatise on detailed methods and techniques of characterization may some day be available. It is probably true, however, that after successfully completing the characterization of a complex, new organic molecule the chemist enjoys a thrill of satisfaction derived in large part from the realization that the sequence of steps used was not given to him in a single reference work but was the result of his own experience, insight, and skill (and perhaps some luck).

The present review of recent contributions in this realm of characterization is concerned with methods for determining purity of samples, procedures for establishing physical properties, and chemical methods of characterization.

PURITY

It is essential for clear-cut determination of properties and for interpretable degradative work that the samples employed be substantially pure. Procedures which are now found most useful for establishment of degree of purity of samples were reviewed recently (*64*, *65*). No fundamentally new methods of these types have been introduced during the past year, but there have appeared a number of papers in which extensions or new applications of method are described.

The development by Craig (*16*, *64*) of a machine for carrying out many-plate countercurrent distributions, and the recent introduction of a convenient glass apparatus for larger numbers of separation stages (*19*, *65*) are now widely recognized. These methods have been introduced in many laboratories and have proved their worth. Continued studies by Craig and his coworkers have culminated in the development of an automatic control device for use with the glass apparatus (*17*). A strictly discontinuous extraction train containing 220 glass equilibration cells may now be operated automatically, so that 800 equilibration stages (about 150,000 extractions) are obtainable in about 24 hours. Using this equipment, a decision on purity of sample may be reached with a considerable degree of certainty. The high resolving power possible with this system is of great importance in cases where more orthodox separations are not feasible by reason of lack of material or instability. It is especially valuable where the homogeneity of sensitive, biologically active principles must be determined.

In chromatographic procedures for determination of purity, various modifications have been reported during the past year. A reversed-phase partition chromatography was described by Partridge and Chilton (*62*), in which powdered glass is used as carrier for a stationary, water-immiscible phase. Craig, Hausmann, Ahrens, and Harfenist (*18*) have discussed application of nests of thin glass shells in a convenient apparatus for drying as an aid in rapid determination of total solids samples. This equipment, easily made in any laboratory, is useful for determination of weight curves in chromatographic column processes, as well as in countercurrent distributions. Extension of theoretical treatment of the chromatographic separation process is much to be desired. Mowery (*56*) has reported data on chromatography using adsorbents of controlled particle size, and working pressures up to 120 pounds per square inch in borosilicate glass columns. Some theoretical considerations are given in this report. Apparatus that will facilitate experimental work should encourage theoretical as well as experimental study. Further reference to chromatography will be found in other papers in this issue.

An apparatus and procedure for separation of a wide variety of charged molecules by continuous electrophoresis and ionophoresis on filter paper, described by Durrum (*24*), provide a method that should prove useful for evaluating homogeneity of samples. The method represents a simplification and modification of the continuous electrophoresis procedure of Svensson and Brattsten (*82*), and permits small scale preparative separations to be carried out in addition to analytical separations.

Additional data on application of differential vapor pressure measurements to determination of purity in a convenient modification of the solubility analysis method were reported by Hughes, Williams, and Young (*38*). The method appears applicable to a variety of compounds.

The importance of caution in the interpretation of paper strip chromatograms for identification purposes (*64*, *65*) is again indicated by observations of Carter, Hearn, and Taylor (*11*), who isolated from streptothricin a substance (Compound A) isomeric with lysine. The two compounds behaved in substantially identical fashion in paper strip chromatograms, but the isomeric compound was shown to be a new diamino-C_6 acid.

PHYSICAL PROPERTIES

Infrared spectroscopy has continued to find wide application in characterization work (*64*, *65*). Most organic compounds yield infrared spectra which provide unique reference data for comparative purposes. Furthermore, such spectra serve to indicate the presence or absence of many functional groups including hydroxyl, amino, keto-, aldehydo-, or ester-carbonyl, carboxyl, and monosubstituted amide. The further application of infrared spectroscopic characterization for structure elucidation is limited only by the scope of accumulated data on various organic structure types. Current work along these lines is exemplified by studies on normal and isosteroids by Josien, Fuson, and Cary (*43*) and on small-ring compounds by Roberts and Chambers (*70*). The assignment of bands to particular structural groupings—e.g., cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl rings—leads to greater usefulness of infrared spectra for recognition of molecule types in biological systems. Grove (*34*) has applied infrared in differentiating between patulin and isoclavacin, and Marion, Lavigne, and Lemay (*52*) found infrared of fundamental help in determining the structure of sedamine. Application of infrared in a quantitative way is further illustrated in analyses of various pharmaceutically active compounds by Parke, Ribley, Kennedy, and Hilty (*61*). Infrared spectra of saturated fatty acids with even numbers of C-atoms from C_6 to

C_{18} were given by O'Connor, Field, and Singleton (*58*). Perry (*67*) has described analysis of mixtures of five C_{10} aromatic compounds by infrared analysis with an error of 0.5%.

Analysis of solids with the mass spectrometer has been considered by Gorman, Jones, and Hipple (*33*). Application of this instrument to determination of nitrogen in organic compounds by Frederickson and Smith (*28*) has given a precision of ±2%. Rock (*71*) has used the mass spectrograph for identification of components of mixtures of organic compounds and has stressed the possibilities of the method.

The microwave spectrograph has been used by Southern, Morgan, Keilholtz, and Smith (*80*) in the isotopic determination of nitrogen and carbon. Only about 0.00015 mole of gaseous product (ammonia, cyanogen chloride) is required; most of this can be recovered. The technique is described in detail, and mention is made of many possible applications for analysis of molecules containing other stable isotopes which can be converted to noncreative gaseous forms.

The contribution of x-ray analysis to solution of problems of molecular configuration of sterols, bile acids, cycloparaffins, and analogous compounds has been discussed by Giacomello (*30*). The use of x-ray diffraction analysis in the identification of solid, crystalline aromatic hydrocarbons is reviewed by Hofer and Peebles (*37*). The investigation of x-ray diffraction behavior of *n*-octadecenoic acids reported by Lutton, Huber, Mabis, and Stewart (*49*) provides further illustration of current applications.

Tabulation of data for Raman spectra of hydrocarbons and oxygenated compounds has been given by Braun, Spooner, and Fenske (*8*). A small scale apparatus for determination of Raman spectra has been described by Mitsushima, Shimanouchi, and Sugita (*55*). Increase of sensitivity has been studied by Vacher (*88*).

Ultraviolet absorption spectroscopy continues to be of value in structural elucidation work. Applications in lignin chemistry are noted in papers by Pew (*68*) and Ritter (*69*), who employ such data for recognition of specific phenolic moieties. Employment of ultraviolet absorption spectra for recognition of acetylenic moieties has been found helpful by Jones (*41*) in work carried out with acetylene compounds in his laboratory. The absorption maxima of the acetylenic residues are so characteristic that Jones was led to suggest the presence of such moieties in agrocybin and related antibacterial substances after seeing the ultraviolet spectra of these compounds (*42*). Ultraviolet absorption of amino acids and proteins and application to analytical investigations have been discussed by Dannenberg (*20*). Other recent applications have been reviewed by Déribéré (*21*).

The measurement of refractive index using as little as 0.25 cu. mm. of a liquid is carried out by Blohm (*4*) with the Abbe-type refractometer by limiting free space by means of tinfoil or aluminum foil and absorbing tissue.

Precise melting point microdeterminations combined with determination of refraction of the melts has been used by Brandstätter (*7*) as a simple means of identifying barbituric acid derivatives. These compounds cannot be readily distinguished by their crystal forms because of poly- and isomorphisms. Microscopic fusion analysis has been applied to sterols by Gilpin (*32*). Since minute quantities of sterols can be easily and rapidly recognized by this procedure, the method should be useful in the sterol field.

Accurate titration of both strong and weak organic bases in various nonaqueous solvents such as benzene, chlorobenzene, nitrobenzene, chloroform, ether, or petroleum ether has been discussed by Fritz (*29*). Perchloric acid in acetic acid was employed and both indicator and glass electrode end points were obtained. Titrations in nonaqueous media have also been studied by Tomicek, Blazek, and Roubal (*85*). Determination of primary and secondary amines in the presence of each other by treatment of the mixture with acetic anhydride or salicylaldehyde prior to titration with acid was reported by Siggia, Hanna, and Kervenski (*76*). Ethylene glycol–isopropyl alcohol is used as solvent. Differential percuprimetric titrations of amino acids and proteins permit certain deductions to be made as to structure, according to Beck (*3*). Microtitration of organic acids using less than 1 mg. of sample was described by Ingold (*39*).

The determination of molecular weight of organic compounds in organic solvents using samples down to 5 mg. in weight with precision equivalent to that of the ebullioscopic procedure has been described by Taylor and Hall (*83*). The solvents do not require rigorous purification. Utilization of the degree of vapor pressure lowering in the determination of molecular weight was reported by Klages and Möhler (*45*). Application of light-scattering studies to molecular weight determination for lactoglobulin, ovalbumin, serum albumin, and lysozyme has been described by Halwer, Nutting, and Brice (*35*).

Determination of molecular weight of peptides by a method of partial substitution—e.g., with dinitrophenyl groups—and countercurrent distribution of the partially substituted mixture has been worked out by Craig (*15*). Because the liberation of acidic or basic groups in peptides or reactions involving substitution of the functional groups of these substances cause striking shifts in partition ratio, countercurrent distribution permits determination of the number of such groups and ultimately the molecular weight of the parent peptide.

Velick and Udenfriend (*89*) have presented in detail their methods of isotope derivative analysis for a number of amino acids. Positive identification is described for proline, valine, methionine, and phenylalanine at the gamma level as *p*-iodophenylsulfonyl (pipsyl) derivatives from protein hydrolyzates. Udenfriend and Velick (*87*) have also given details of the isotope derivative method as applied to determination of amino acid and groups in proteins.

Application of the stable isotope dilution method to determination of nicotinic acid by Trenner, Walker, Arison, and Trumbauer (*86*) provides an absolute assay for nicotinic acid in complex mixtures. This work is a further illustration of the importance of the isotope dilution principle in the development of specific (absolute) assay methods.

A review of micromethods of determination of physical constants has been presented by Sobotka (*79*).

CHEMICAL PROCEDURES

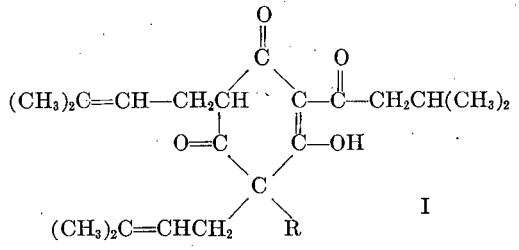
Quantitative aspects of functional group determination in characterization of organic compounds have been discussed by Siggia (*75*). Determination of functional equivalent weight by functional group analysis, verification of suspected identity, and other applications are considered. A useful summary of methods for detection, characterization, and estimation of functional groups has been given by Viebel (*92*). The estimations are generally based on a titrimetric method. These procedures appear to be representative of those comprising a practical course in identification of organic compounds for graduate students in the Technical University, Copenhagen, Denmark. Indication of a trend in quantitative functional group determinations is seen in the microanalytical use of lithium hydride by Schöniger (*74*).

A qualitative color test for aromatic nitro and nitroso groups using lithium aluminum hydride followed by addition of aqueous sulfuric acid has been developed by Gilman and Goreau (*31*). The colors produced range from brown through yellow, orange, and red. Nelson and Laskowski (*57*) have also used lithium aluminum hydride as a qualitative test reagent for aromatic nitro groups. Another color test for nitro groups employing a sodium nitroprusside reagent or sodium pentacyanoaminoferroate after reduction was described by Okuma (*59*). The colors obtained may be purple, green, or blue. A color reaction for methyl ketones was reported by Adachi (*1*). The substance is treated with hypochlorite or hypobromite and pyridine and heated to boiling. Compounds giving positive iodoform tests show a pink or carmine color in this test. Sakaguchi (*72*) has described a modification of the colorimetric determination of arginine.

Organic acids may be converted to *p*-bromo- and *p*-phenylphenacyl esters in good yield by means of *p*-bromo- and *p*-phenyl-α-diazoacetophenones, according to Erickson, Dechary, and Kesling (*26*). Cupric chloride is used as a catalyst. No lachrymatory products are involved, in contrast to the case with phenacyl bromides. Characterization of esters of aromatic acids and aliphatic dicarboxylic acids by means of *N*-(β-aminomethyl)-morpholine was found by Bost and Mullen (*5*) to give good yields of pure, crystalline, stable derivatives whose melting point spread was wide enough to ensure complete identification. The tertiary nitrogen atom present enables the molecule to undergo quaternization with ease, thus affording a second derivative of the ester in doubtful cases. Bost, Starnes, and Wood (*6*) reported the use of 2,4-dinitrophenol as a reagent for characterizing a wide variety of halo compounds including alkyl halides, halohydrins, halonitriles, haloesters, haloketones, and haloethers. Crystalline products are easily obtainable.

Microgram-scale identification of triphosphoric acid esters of thiamine by employment of quinine molybdate as a reagent and by examination under Wood's light has been described by Velluz and Pesez (*90*). The method could probably be used for differentiation of analogous compounds.

Alkaline fusion reactions and alkaline degradations have been very useful in structural elucidation work for a long time. A few recent examples are given. Alkali fusions of terramycin and aureomycin yielded salicylic acid and 5-chlorosalicylic acid, respectively, in structural studies on these antibiotics conducted by Kuhn and Dury (*47*). More detailed alkaline degradative studies on terramycin have been carried out by Pasternack, Bavley, Hess, and Conover (*63*) and by Hochstein and Pasternack (*36*). Alkaline degradation was employed in structural studies on humulone (I, R = —OH) and lupulone [I, R = —CH_2—CH=$C(CH_3)_2$] by various workers including Wieland (*93*), Wieland



I

and Martz (*94*), Wollmer (*96*), Cook and Harris (*13*), and Verzele and Govaert (*91*). The value of alkaline degradation is diminished in a case such as this by reason of the possibility of double bond migrations. Verzele and Govaert established the cited structures of humulone and lupulone by employing ozonolysis (*91*). Carson (*10*) has recently confirmed these observations in his ozonization studies. Good recovery of acetone and of methyl *n*-propyl ketone from the volatile products was accomplished via chromatography of the 2,4-dinitrophenylhydrazones on silicic acid.

The apparently specific action of osmium tetroxide in combining with steroids possessing an α,β-unsaturated 3-ketone group has been suggested by Manaro and Zygmuntowicz (*51*) as of potential value in detection and characterization of steroids in extracts of biological fluids. Recent advances in characterization of steroids in general are not included in the present paper.

Stepwise degradation of peptides, elucidation of molecular weights of peptides and smaller peptide fragments from hydrolyses, determination of amino acid sequence, identification of amino acid residues, and characterization of the free functional groupings present in peptides have been extensively studied. Application of dinitrofluorobenzene (DNFB) as a labeling reagent to introduce the dinitrophenyl (DNP) residue into peptides, and utilization of repetitive countercurrent distributions of the dinitrophenyl peptides have been employed by Craig (*15*) to determine molecular weights. Partial hydrolyses have been followed by ion exchange chromatography, charcoal adsorption, and paper chromatography in methods reported by Sanger (*73*). Enzymatic hydrolysis could be successfully studied by these methods.

Destruction of dinitrophenyl amino acids when refluxed in solution in the presence of tryptophan was noted by Thompson (*84*). In the absence of tryptophan no destruction was observed. Regeneration of short- or long-chain amino acids from their dinitrophenyl derivatives may be accomplished by heating the latter with ammonia in sealed tubes at 100° for 2 hours, according to Lowther (*48*). The resulting solution is acidified and extracted with ether, leaving an aqueous solution of the amino acids. The method is useful in conjunction with paper strip chromatography.

Further experiments with phenylthiocarbamyl derivatives of peptides in stepwise degradation studies have been carried out by Edmann (*25*). Stepwise degradation of peptides by treatment with ethyl methyl xanthate to give an *N*-thiocarbethoxy derivative, followed by removal of the terminal amino acid as the thiazolid-2,5-dione, has been described by Khorana (*44*). The terminal amino acid can be recovered from the thiocarbamic acid after treatment with hydrochloric acid. The *N*-thiocarbethoxy products examined were usually crystalline, and yields were reported to be good. Quantitative reaction of a peptide with carbon disulfide has been used by Cook and Levy (*14*) for peptide degradation on a micro scale. By means of a self-recording "pH-stat," and kinetic analysis of the data thereby obtained, the number of free α-NH_2, ε-NH_2, α-NH<, and —SH groups in the molecule could be separately computed. Acidification of the peptide dithiocarbamate gives the thiazolidone of the terminal amino acid together with the peptide minus the latter amino acid.

Microdetermination of end groups in peptides by reductive methylation of the free amino end group has been described by Ingram (*40*).

A simple rapid spectrophotometric method for determination of amino acids and peptides was reported by Spies and Chambers (*81*). The method involves reaction with a copper salt, and is based on the color obtained when the combined copper is converted to the copper salt of alanine. This procedure has been applied in a study of rate of protein hydrolysis.

Paper chromatography of peptides has been extended by Knight (*46*). A method for calculation of the R_F value of any desired peptide was given by Pardee (*60*). This calculation depends on the R_F values of the component amino acids and two experimentally determined constants. Average accuracy is reported to be excellent.

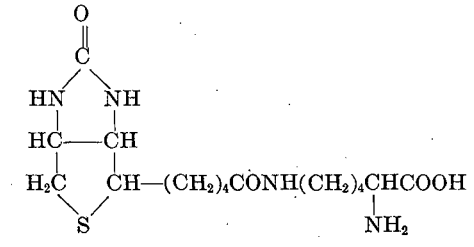
Elucidation of structure of the *Lactobacillus bulgaricus* factor,

$$HOCH_2C(CH_3)_2CH(OH)CONHCH_2CH_2CONHCH_2CH_2SH$$

II

II, by Snell *et al.* (*78*) included experiments with nitrous acid to demonstrate absence of any free primary amino group. Use of this reagent by Peck, Wolf, and Folkers (*66*) in structural

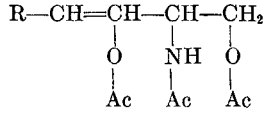
III



work on biocytin, III, was employed in elucidation of the position of the amino group of lysine involved in the linkage with biotin. Hydrolysis of the nitrous acid reaction product yielded a lysine degradation product which gave no ninhydrin reaction for primary α-amino nitrogen under the conditions employed.

Catalytic hydrogenation of triacetylsphingosine, IV, was shown by Carter and Humiston (*12*) to give two products. One

was the expected compound resulting from hydrogenation of the carbon-carbon double bond. The other product appears to have been derived by hydrogenolysis of the allylic acetoxy group prior to hydrogenation of the original double bond. This type of hydrogenolytic cleavage may be encountered in other structural elucidation work.



IV

Periodate oxidation was used by Drummond (*23*) in establishing the structure of lasiocarpic acid, $(CH_3)_2C(OH)C(OH)$—$(COOH)CH(CH_3)(OCH_3)$. The formation of acetone, demonstrated as one of the oxidation products, was conclusive evidence of the structure shown. Periodate oxidation was used by Wolfrom, Montgomery, Karabinos, and Rathgelo (*95*) in structure work on heparin to show the presence of one α-glycol group per disaccharide unit of this molecule. This paper provides an illustration of application of countercurrent distribution and electrophoretic methods for establishment of homogeneity of an amorphous substance, as well as showing utility of periodate.

A new case of resistance to periodate oxidation of adjacent hydroxyl groups was observed in D-glycosan <1,4> α <1,6> by Alexander, Dimler, and Mehltretter (*2*). Failure of periodic acid to react with polyhydroxy compounds under the usual analytical conditions has generally been accepted as proof of the absence of vicinal hydroxyl groups. Two previous reported examples of compounds containing adjacent hydroxyl groups which failed to react with periodic acid are D-glucosan <1,4> β <1,6>, studied by Dimler, Davis, and Hilbert (*22*), and D-glucosaccharo-1,4-lactone, examined by Smith (*77*). This failure of oxidation is thought to result from the relative trans arrangement of the adjacent hydroxyl groups and from the structural rigidity resulting from introduction of a double ring system into the molecule. Caution in interpretation of negative periodate oxidation as evidence of the absence of 1,2-glycol groupings is indicated by these observations. The influence of stereochemical configuration on rates of oxidation by glycol-splitting reagents is discussed by McCasland and Smith (*50*). Lead tetraacetate and periodate oxidations of aminocyclanols were studied. Data on influence of pH on oxidation rate by periodate are given. Determination of glycolic acid by means of chromotropic acid provides a semimicromethod applicable in periodate oxidation studies, according to Fleury, Courtois, and Perles (*27*).

Application of enzymatic cleavage to linkage studies on ribonucleic acids has been discussed by Markham and Smith (*53*). The action of the enzyme could be shown to be similar to that of controlled alkaline hydrolysis. In selected cases, enzyme cleavages may be found very useful in structural elucidation of biologically active substances.

Microbiological assays specific for certain individual chemical compounds are finding continued application in identification work. A recent method reported by Camien (*9*) for specifically determining either D- or L-aspartic acid at will using *Leuconostoc mesenteroides* illustrates one such method. Another is seen in the quantitative decarboxylation of the β-carboxyl group of L-aspartic acid to give L-alanine catalyzed by *C. welchii*, in experiments reported by Meister, Soher, and Tice (*54*).

CONCLUSION

Methods for characterization of organic compounds are of fundamental importance in the solution of many of the problems confronting the chemist in synthetic and degradative organic work and in biochemistry. Wherever possible, "classical" organic procedures should be employed in identification of organic compounds. Novel techniques—paper chromatography, specific microbiological assays, immunochemical reactions, and the like—have a significantly increasing role in elucidation of identity and structure. The continued isolation of new, complex organic compounds from natural products makes necessary a continuing search for new characterization methods and refinements of older techniques.

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EXPERIMENTAL STATISTICS

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THE utility of modern statistical techniques for handling experimental data continues to be increasingly appreciated by research workers in the physical sciences. The literature grows exponentially. Literally, hundreds of articles on statistics have appeared since the earlier review on this subject by Wernimont (January 1949) (*135*). Only a modest fraction of these has been included here. In making a selection the authors have taken the position that, by and large, this review is intended to serve those having, at most, a nodding acquaintance with statistical methods. Consequently, they have leaned heavily on expository articles, trying especially to pick those with a predominantly chemical flavor. More advanced and purely technical articles have been purposely omitted, as it was felt that a relatively small group would be interested in such papers. Most of these people will already be well acquainted with the statistical periodicals and, consequently, will have much less need for a review of the type given here.

On the other hand, they have also omitted a large class of papers in which statistical methods have been used to analyze experimental data, but in which the emphasis has not been primarily on these techniques as such. Though these articles could not be included, it was indeed gratifying to find such widespread use of the various statistical tools.

OTHER BIBLIOGRAPHIES

This review is intended as a continuation of Wernimont's article (*135*). Wernimont also deserves a large measure of credit for his assistance on this paper. He furnished a set of some 300 reference cards, from among which the majority of selections were eventually made.

Several other statistical bibliographies should be called to the readers' attention. The first of these is the very recent Wiley publication edited by Buros (*18*). This consists of reviews of 342 statistical methodology books and pamphlets written in the 10-year period indicated. Buros' book, plus the book review section of the *Journal of the American Statistical Association*, provides a fairly complete coverage of the nonperiodical literature.

In the field of quality control Butterbaugh's "Bibliography of Quality Control Literature" (1946) (*21*) and its Supplement (1951) (*22*) are most comprehensive. A running bibliography in *Industrial Quality Control* covers the period from 1949 to date.

So far as is known to the authors, these represent the principal bibliographical sources likely to be useful to chemists and other physical scientists.

BOOKS

Theory. Several books are devoted primarily to statistical and/or probability theory (*24, 48, 59, 92, 97, 131*).

Methodology. Books in this group are devoted either entirely to techniques or to a combination of theory and practice (*8, 14, 18, 22, 27, 34, 40, 53–56, 60, 77, 84, 96, 103, 105, 122, 123, 125, 126, 129, 139, 141, 151, 154*).

PRECISION, ACCURACY, AND RESOLUTION OF ERRORS

In this section are included articles on precision, accuracy, and closely related topics (*4, 23, 28, 35, 62, 64, 68, 71, 81, 90, 119, 121,*

127, 134, 137, 138, 144, 145, 150, 152, 153). In the past two or three years there has been a considerable upsurge of interest among statisticians in the subject of "components of variance." In chemical applications the term "resolution of errors" is perhaps more appropriate. This subject is concerned with the estimation of the relative importance of different sources of variability contributing to the over-all errors. An example of how much can be accomplished in this direction is given by Weybrew, Matrone, and Baxley (*137*), though unfortunately the calculations are not shown.

An important phase of the variance components problem is that of separation of errors of measurement and inherent product variability when repeated measurements on the same item are not possible—e.g., destructive tests. To achieve this separation, it is necessary to be able to make simultaneous observations with two or more measuring devices. The papers of Grubbs, Smith, and Whitwell discuss this technique (*71, 119, 138*).

CURVE FITTING

Relatively few research workers in the physical sciences are aware of the elaborate and powerful theory that has been developed in connection with curve fitting. Substitution of objective criteria (principally that of least squares) for rule of thumb procedures has been merely the first step. Use of fitted curves to predict future values of a dependent variable gave rise to techniques for evaluating the expected errors of such predictions. When basic structural relationships are being estimated we need some measure of the reliability of our estimates. Confidence intervals for parameters in such relationships have been found. The curve fitting techniques have been generalized to include several independent variables simultaneously. Statisticians often refer to this whole subject as "regression." For elementary expositions, the Brownlee and Olds papers are suggested (*6, 9, 13, 32, 43, 74, 101, 107, 130*).

DESIGN OF EXPERIMENTS

In all probability, the most important contribution that statisticians have to make to the advancement of science is in the field of experimental design. Many phases of this subject are nothing more than the exercise of a good measure of common sense in the planning stage of a research program. Decisions must be made on the size and scope of the program, the factors to be investigated, and the type of data to be gathered. One must carefully consider what questions the experiment will be capable of answering. He must be sure the factors being investigated do not become confounded with each other or with some extraneous variable. He must make an effort to get precise and accurate measurements. Indeed, it is usually advisable to have a method for estimating precision built into the experiment. Design of experiments, however, goes considerably beyond these basic considerations. Having done what one can to remove extraneous sources of variation and to make measurements as precise as possible, one can frequently decrease the effective experimental error dramatically by the application of ingenious arrangements within the experimental program. A considerable variety of such arrangements (designs) has been worked out in the fields of agriculture and biology. Many of these can be carried out equally well in the chemistry laboratory. Systematic methods of statistical analysis (analysis of variance and covariance) are available for these designs.

So-called factorial experimentation is particularly being emphasized in the literature. In investigating the effects of several factors, say time of reaction, temperature, concentration, etc., on a process, the traditional approach has been to vary one factor at a time, the others being temporarily held constant. The modern approach is to investigate all possible combinations of the various levels of the factors. Its principal advantage is in the detection of so-called interaction effects. In many cases, an investigation involving all possible combinations would be prohibitively large; however, there now exist systems of constructing so-called "fractional factorials" in which the number of combinations is drastically reduced without sacrificing any important information (*5, 27, 36, 50, 66, 76, 88, 100, 104, 106, 111, 133, 148*).

BIOLOGICAL ASSAY

The statistical techniques useful in bioassay work are set forth in some detail in Finney's book (*53*). In addition several recent contributions to the periodical literature are listed (*7, 15, 16, 41, 51–53, 65, 83, 91*). The authors would like especially to call attention to the usefulness of many of these techniques in fields considerably removed from bioassay—e.g., in the testing of sensitivity of explosives, in plastics life tests, etc. The characteristic feature of data amenable to treatment by these methods is that the response of each individual specimen to a given stimulus is measured only as being either positive or negative, the outcome in each case depending on whether or not the stimulus exceeds an unknown threshold value for the specimen.

TEACHING OF STATISTICS

An increasing amount of attention is being given to the problem of providing formal statistical training for the student in engineering and the physical sciences (*45, 67, 102, 117, 120, 142*). The authors, and many of their colleagues, take the position that eventually a sequence of courses in modern statistical concepts and methodology will be regarded as indispensable in the curriculum, as are the basic mathematics courses at present. They feel the objective should be a generation of statistically minded engineers and physical science research workers, rather than a large group of professional statisticians.

QUALITY CONTROL

The subject of quality control has enjoyed a phenomenal growth since the early war years (*2, 3, 8, 12, 19, 21, 22, 29, 58, 61, 63, 80, 82, 98, 103, 108, 110, 114, 116, 126, 128, 136*). It is one of the simplest, yet most useful of all the statistical techniques. Though not restricted to large scale manufacturing operations, it has thus far found the bulk of its applications in this connection. Basically, statistical quality control consists of keeping a graphical record of some quality index. On this so-called "control chart" are drawn certain "control limits" whose function it is to call attention to abnormal quality variations. When properly placed, these limits make the distinction between quality variations inherent in the manufacturing technique and variability which calls for corrective action.

The place of the control chart technique in research investigations has, thus far, received all too little attention. Almost all of the common statistical techniques are based on the tacit assumption that the data can be treated as a random sample from a stable probability distribution. Control charts provide a simple method of checking on this assumption. It is frequently the case particularly when the data have been gathered over a period of several days, that the assumption of stability becomes untenable. An excellent discussion of this subject is given by Shewhart (*114*). This reference appeared in the Wernimont review, but is worth repeating here.

MISCELLANEOUS

In this review, the authors have attempted to give separate lists of articles for several special topics within the general field of statistics. They hope that this has been a convenience. The remaining papers are included in this miscellaneous category (*1, 7, 10, 11, 17, 20, 25, 26, 30, 31, 33, 37–39, 42, 44, 46, 47, 49, 57, 69, 70, 72, 73, 75, 78, 79, 85–87, 89, 93–95, 99, 109, 112, 113, 115, 118, 124, 132, 135, 140, 143, 146, 147, 149*). They cover a very wide variety of subjects, as is evident from their titles. In some instances, individual papers deal with as many as four or five different techniques.

Finally, the authors would like to single out for special com-

mendation the publication of statistical symposia in various periodicals. Several very fine examples of these have appeared recently in ANALYTICAL CHEMISTRY, in *Industrial and Engineering Chemistry*, in the *Proceedings of ASTM*, and in the *Annals of the New York Academy of Sciences*. This technique is believed to be one of the best available for arousing interest in statistics on a really large scale.

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BIOCHEMICAL ANALYSIS

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IN A previous review of this subject (*139*), the authors stressed the fundamental differences of biochemical and ordinary chemical analysis. These differences emphasize the importance of the preparative as compared with the determinative phases of the analysis, the fractionation as compared with the determination. Because of the great extent and wide ramifications of the subject, the subdivisions reviewed were chosen somewhat arbitrarily and on the basis of the best evaluation available at the time. The developments of the two intervening years have confirmed the choices made then, with a few possible minor exceptions. The main topics discussed have developed in importance or have continued their importance without interruption. Accordingly, the topics chosen here for discussion are largely those that were included previously, along with some additional analytical techniques that were not discussed earlier. Because most of the significant techniques of the biochemical analyst are also important in other fields of chemistry, considerable duplication and repetition of other review material are inevitable.

Analysis, though fundamental to biochemical progress, has received far less attention from biochemists than it deserves. Biochemical training rarely includes sufficient consideration of analytical chemistry, because the requirements in other phases of chemistry and biology are so extensive. This deficiency of training has led to many analytical shortcomings in the biochemical literature and in practice, in both routine and research analysis. Perhaps the outstanding example is in the field of clinical analysis, which has been influenced more by the requirement for speed than for either accuracy or dependability. Its deficiencies have often been justified on the ground of a large "biological variation" which is supposed to cover any degree of variation that happens to exist in the currently employed method in the particular laboratory. The true biological variation has probably never been determined for most constituents because methods accurate enough to determine it have been largely lacking and rarely applied. It is a hopeful sign that renewed interest in this important phase of biochemical analysis is awakening in the form of a re-examination and evaluation of the magnitude of the problem. Thus, Belk and Sunderman (*11*) and Snavely and Golden (*257*) have conducted surveys of clinical laboratory operation which have brought to light errors that are far larger than those usually assumed and often so large as to invalidate the utility of the results. Such studies as that of Shore and Thomson (*251*) of total error in widely employed methods are becoming more numerous and point to improvement in this matter. Perhaps a referee system such as that of the Association of Official Agricultural Chemists might be established to control the more serious deviations. Unfortunately research workers, though more competent and careful than routine analysts, also have fallen into serious analytical pitfalls. Realization of these facts, and interest in their correction, may be expected to produce continued improvement.

FRACTIONATION OF BIOCHEMICAL SYSTEMS

Separation of biochemical systems into their constituents remains one of the most necessary and difficult of analytical operations because of the complexity of the systems, the lability of their components, their extensive interaction, and the close similarity of the constituents of a group to each other. An important trend has been toward determination of constituents *in situ*, thus avoiding the necessity of separating and altering the sample material.

DIFFERENTIAL CENTRIFUGATION

The past two years have seen the acceptance in principle of the process of centrifugal fractionation of cell materials by biochemists, generally. The technique has remained identical in fundamentals, although more precise media and fraction evaluation techniques have developed.

The separation and properties of cell components by this method have been discussed by Hogeboom (*120*). Developments in determination of enzyme locale have been reported (*243*) and the progress in the field has been examined critically (*221*).

CHROMATOGRAPHY

The techniques of paper partition and column chromatography, including ion exchange, have emerged as indispensable and almost universally applicable tools for biochemical analysis (*304*). Their routine and research applications are so numerous and varied as to place detailed consideration out of the scope of this review. Several trends have become apparent:

Considerable standardization of method has been achieved in the separation of common constituents such as the amino acids.
Basic understanding of the processes has been furthered by fundamental research, as compared with empirical research only, though this is still the rule.
New techniques, approaches, and applications have been numerous.
Combinations of the chromatographic techniques with each other and with other analytical operations are becoming more common and producing highly significant results.

It is with these trends that the present review is particularly concerned.

Ion Exchange. Ion exchangers have long been used for removal of inorganic ions from water and industrial solutions, but in recent years they have become a very powerful tool for biochemical separations. This development depends on the fact that many very significant components of the biological system such as proteins and their hydrolysis products, components of nucleic acid, and other organic substances are normally ions in their natural state or can be converted into ions at some practical pH. Adsorp-

tion on an ion exchange resin, followed by fractional elution, has produced separations with an efficiency unobtainable by non-chromatographic methods. Thus, three isomeric adenosine phosphates were separated by Cohn and Volkin (*61*). While fractionation of adenosine phosphates from similar uridine phosphates may be explained in terms of charge difference, the separations of isomeric adenosine phosphates from one another implies that ion exchangers, like the classical adsorbents, discriminate among ions of like charge but differing structure.

Some additional illustrations of the wide applicability of ion exchange materials to biochemical analysis are given by the work of Cohn (*56, 57*) and Cohn and Carter (*59, 60*), who have greatly extended the knowledge of nucleotide fractionation, as have also Loring and coworkers (*172*). A new amino acid, α-methyl-β-alanine, was isolated from human urine by employment of ion exchange resin by Crumpler *et al.* (*74*). Bergström and Hansson (*14*) purified adrenaline and histamine in this manner, while Jackel, Mosbach, and King (*126*) separated ascorbic acid and isolated its 2,4-dinitrophenylosazone. Cohen and Scott (*55*) separated pentose phosphate from 6-phosphogluconate with a strong base anion exchanger. One of the more striking applications of ion exchange was made in purifying enzymes including ribonuclease, lysozyme, and cytochrome c (*117, 187, 198, 208*), which could be separated and in some cases divided into more than one constituent.

Routine application of ion exchangers in analytical separation problems might be illustrated by the work of Applezweig (*3*), Mukherjee and Gapta (*201*), and Jindra and Pohorsky (*128*), who employed ion exchange columns in the separation and analysis of plant and pharmaceutical materials for the alkaloids; St. John, Flick, and Tepe (*237*), who separated streptomycin and mannosidostreptomycin in fermentation broths prior to spectrophotometric determination; or Reid and Jones (*229*), who fractionated the proteins of blood plasma by reducing the ionic strength with ion exchange resins. A similar study was made by Sober *et al.* (*258*) with mixtures of egg white protein, in which the ion exchange column was used in conjunction with the electrophoresis apparatus. Marcus (*183*) deionized the protein-free filtrate of body fluids to remove interfering ions preliminary to the determination of lactic acid. An interesting application of ion exchange was that of Isbell (*125*), who estimated carbonyl groups by combination with radioactive cyanide, adsorption on basic ion exchange resin, elution, and measurement of the distribution radiometrically. Applications to analysis of amino acids and other biochemical constituents have been fairly common (*28, 62, 64, 76, 212*). A comparison with the well validated starch column method (*262*) emphasized the great value of ion exchange methods for the analysis of the amino acid composition of proteins.

Fundamental studies of the more useful ion exchangers were made by Wheaton and Bauman (*288*), Lindsay and D'Amico (*167*), Hale and Reechenberg (*109*), Kressman and Kitchener (*145*), Duncan and Lister (*82*), Kunin and Myers (*152*), and Partridge (*211*). The entire field of ion exchange has been well reviewed by Kunin (*149–151, 153*) and its general analytical applications have been covered in considerable detail by Schubert (*244*) and Tompkins (*274*).

Column chromatography employing adsorbents has made notable progress but less strikingly than either ion exchange or paper chromatography. As is true also of ion exchange columns, the obvious advantage of being able to separate relatively large quantities of material must lead to continued employment of this type of separation. Perhaps the most notable developments in this field have been those of Tiselius and his coworkers (*121, 272*), who have used carbon columns extensively as well as silica gel and other adsorbents to separate adrenocorticotropic peptides (*166*), proteins (*250*), and other materials. Charcoal and silica gel have been found useful for the interesting application to separation of gases (*72*) which may be analyzed by thermal conductivity after elution with hydrogen, or gases may be separated and detected with suitable indicators impregnated in the solid carrier (*107*). Adoption of alumina columns has apparently increased as compared with other adsorbents. They were found very effective for separation of steroids (*228*); they allowed the isolation of very small quantities of vitamin A for its spectrophotometric determination (*119*), the identification of most of the products of potato starch hydrolysis by malt amylase (*279*), and the quantitative determination of *p*-hydroxyphenylpyruvic acid as a test for liver function (*138*), among many other applications.

A number of interesting uses of other adsorbents have been reported; silica gel columns for separation of tetramethyl-, trimethyl-, and dimethylfructoses with a 90 to 98% recovery (*240*); 2,4-dinitrophenyl derivatives of amino acids on a reversed phase chlorinated rubber column (*213*); and amino acids on powdered cellulose (*19*). Significant advances in technique or theory of column chromatography have been reported by several investigators (*31, 115, 164, 196*), and a self-contained column or "chromatobar" has been described (*193*) with which the reagent used for development can be applied directly to the outside of the column to locate bands, after which they can be separated. The adsorbent used—e.g., silicic acid—is mixed with enough plaster of Paris to form a solid bar, reinforced by a central glass rod. Its operation was checked by separating and identifying a number of volatile flavoring constituents of citrus fruits.

Paper Partition Chromatography. This technique has become approximately as standard in biochemical laboratories as colorimetry or titration. Perhaps never in history has a technique, neglected for decades, suddenly assumed the importance and universal acceptance that has been accorded this technique. The reasons are evident; the great simplicity of the equipment and technique combined with the delicacy and reproducibility of the method and its tremendously wide application have amply justified its wide adoption. To review the field in detail as it affects biochemical analysis is next to impossible. Numerous general reviews of technique and application are already available (*24, 25, 102, 131, 186, 263*). It is sufficient here to note some of the more important and unusual developments that may indicate the trends and the direction of increased future application. Only a short time ago, paper chromatography was considered almost entirely in terms of separation of amino acids, as this was one of its early triumphs. This work continues on a broad front with the acquisition of more information about the occurrence of amino acids and the composition of the proteins in terms of amino acids than was conceivable just a few years ago.

Analyses have been performed with natural products such as tissue and urine, in which new or unusual materials have been demonstrated (*90, 205, 268*); and correlations have been found with pathological conditions (*46, 90, 231*). Li and Roberts (*165*) determined the amino acids of mitochondrial fractions of tissues. Some otherwise difficult analytical problems of analysis have been solved—e.g., Smith and Moxon (*255*) separated sulfur-containing amino acids from their selenium analogs, and Butler (*44*) separated glutamine and asparagine and determined them separately with simple technique. Polson (*219*) studied the separation of amino acids belonging to homologous series. Perhaps more studies have been made of amino acid and peptide-containing systems with paper chromatography (*5, 13, 17, 18, 20, 37, 38, 75, 94, 98, 135–141, 146, 159, 195, 209, 215, 253, 298*) than with any other type of component. The consistent effort to improve the accuracy of quantitative determination of the separated components of amino acid and peptide-containing systems has continued with some success (*93, 217, 297*). Some destruction of amino acids on paper during separation and determination has been shown to occur (*36, 93*), as has extraction of amino acids from plasma by petroleum ether during removal of fat (*302*). Careful and useful studies of different papers and other materials and techniques for employment in separating amino acids have been made (*143, 273*) and an interesting technique of retention

analysis on paper has been developed (*291, 294*). Khorana (*137*) employed paper chromatography to study end groups of peptides as the 2,5-thiazolidinedione derivatives. Some success has been reported in the separation of proteins and enzymes by paper chromatography (*95, 126, 129, 252, 301*), though ionophoresis would appear to be a preferable technique, as discussed below.

Many studies of carbohydrates, glycosides, and their derivatives by means of paper chromatographic separations have been made (*2, 39, 123, 127; 140, 142, 157, 181, 192, 214, 224, 235, 275, 283, 284, 295, 299*). Purines, pyrimidines, and the corresponding nucleotides and nucleosides have been separated by paper chromatography in several laboratories (*47, 160–162, 185, 197, 226, 256*), though with perhaps less success for quantitative study than by ion exchange columns. Much attention has been given to the separation and analysis of the difficultly separated organic acids (*12, 27, 33, 34, 49, 105, 118, 134, 188, 222, 238, 260, 290*) including keto acids (*179, 180, 292*). Other difficultly separated materials of biochemical interest in which the paper chromatographic technique has been uniquely useful include steroids (*42, 43, 114, 147, 177, 206*); adrenal hormones (*234, 249, 284, 303*); nonsugar polyhydric alcohols, which could be separated from sugars and identified (*122*); porphyrins (*53, 204*); various vitamins and closely related products (*108, 124, 178, 182, 300*); and alkaloids (*173, 191, 202, 245*). Some particularly interesting uses of paper chromatography have been in separating growth factors (*112*); isolation of a fluorescent material from the larvae of *Bombyx mori*, believed to be a tetrahydroflavone (*81*); in studying isotope-labeled antigen-antibody reactions (*296*); and in separating phosphate esters containing tracer phosphorus (*29*). Burma and Banerjee (*40*) have shown that paper is not entirely passive in chromatography, but exerts some adsorptive effects that can be readily demonstrated. Treatment of the paper with certain chemicals will alter its properties to behave more like an ion exchange material (*236*). Paper, in the form of disks, pulp, or powder may be made to operate in a column (*41, 305*), and it is sometimes impregnated with solid adsorbents such as alumina (*92*) which impart to it a different degree or kind of adsorptive properties. By treatment with silicone, Kritchevsky and Tiselius (*148*) reversed phases in paper partition chromatography, thus making it more suitable for steroids which have very low water solubility. This might develop into a more general method for separating hydrophobic materials.

IONOPHORESIS

Chromatographic procedures have occasionally been useful in purification of unusually stable proteins such as ribonuclease or lysozyme. Chromatography may be used in deionization of protein solutions, and in decalcification of blood plasma. In general, these procedures are not directly responsible for protein isolation or purification. In efforts to develop other techniques for protein and peptide separation, numerous attempts have been made to use electrophoresis in the presence of silica or agar gel or on paper sheets. The use of such methods in a supporting medium of silica gel (ionophoresis) has proved efficient and indispensable (*62, 63*). However, silica gel interacts with many proteins to prevent the desired transport (*103*). While materials such as glass wool (*65*) and asbestos fiber (*45*) may be used in certain techniques, the use of agar gel (*103, 104, 216*) as supporting medium in trough or Vycor tube (*216*) should prove more versatile.

Electrophoresis on filter paper strips or sheets has been rapidly exploited by several groups of workers, so that three years have already established many features of its technique and limitations. The use of filter paper for electrophoretic separations was first demonstrated by Wieland and Fischer (*291*). A variety of experimental approaches has developed, as attempts to control variables inherent in the process have been made. Apparatus has varied from a simple suspension bridge of paper (*194, 291*) to ridgepole suspension (*83, 85*), to flat paper strips in a closed system (*174*), and flat strips or sheets between glass plates (*73, 155*).

While the most efficient apparatus for paper electrophoresis has probably not yet been developed, the trend is represented in the designs of McDonald (*174*) and Kunkel and Tiselius (*155*), with personal judgment favoring the latter. While many variables received attention in previous procedures, the work of Kunkel and Tiselius would seem to provide a rational basis for work of this nature. These workers demonstrated that the migration of nonelectrolyte, dextran, gave a measure of electro-osmotic migration of solvent. Correct and routine determination of this migration is a prime necessity in the comparison of mobility of a given substance on paper with the mobility in free solution. The apparatus of Kunkel and Tiselius also provides for minimal evaporation of solvent, eliminates siphoning from one buffer cell to the other, and protects migrating material from unfavorable pH or redox conditions due to accumulation of electrode products. This protection is provided by comparative isolation of the electrodes in distant reaches of the buffer cells. The mobility of replicate samples of human albumin, after correction for electro-osmosis and devious migration path, agreed in order of magnitude with the mobility of this albumin in free solution.

The various paper electrophoresis techniques have been applied to fractionation of mixtures of inorganic ions (*144, 158, 175*), amino acids (*16, 64, 65, 83, 85, 86, 291, 293*), proteins (*73, 85, 103, 104, 106, 155, 241, 242, 246, 277*), and enzymes (*194, 285*). It seems apparent that variations in apparatus may be insignificant for empirical fractionation of desired solutes. The fractionation on the basis of charge or mobility differences with minimal chromatographic effects seems to rely chiefly on the work of Kunkel and Tiselius (*155*). A large element of chromatography would seem present in the techniques of Durrum (*83, 84*), for example.

Combinations of chromatography and electromigration have been attempted by a number of workers, in the hope that rapid and continuous separations would result. Discontinuous separations on paper were effected by Haugaard and Kroner (*113*). Svensson and Brattsen (*267*) utilized a cell filled with small glass beads, with solvent flowing continuously, for the separation of dyes.

Strain (*264*) and Strain and Sullivan (*265*) have developed a controlled system of separation of inorganic ions on paper, with simultaneous downward solvent flow, horizontal electrophoresis, and continuous sample collection. Durrum (*84*) has announced a similar but not identical system, using free hanging paper rather than paper between glass plates (*265*). Durrum's apparatus thus provides less protection against solvent evaporation, but isolates electrode products to a greater extent.

While the fields of paper electrophoresis and vector electrophoretic chromatography are infants, it seems safe to predict that these fractionation systems will become of paramount importance in the isolation of small quantities of homogeneous protein and peptide fractions, as well as fractions of other charged "biological" molecules.

COUNTERCURRENT DISTRIBUTION

The countercurrent distribution technique of Craig has shown steadily increasing application in biochemical studies. The necessity of using special apparatus of some complexity, and considerable time consumption have been deterrents to its general adoption as compared with the simpler chromatographic techniques, but its advantages in terms of general applicability, range of sample content, and exact interpretation argue for its increasing importance. The technique, theory, and some of the biochemical applications have been reviewed (*66, 67, 101, 133*).

The application of the technique has been extended by development of improved apparatus capable of making many more transfers than in the original equipment, even automatically. Fischer and Juberman (*91*) described an all-glass apparatus with which they studied 5-component systems in a 30-stage device. Significant changes in design to allow more extraction stages without great increases in time and labor have been described by Craig;

and Post (*70*) and more recently by Craig, Hausmann, Ahrens, and Harfenist (*69*), who have developed an automatic glass extraction train capable of performing some 800 equilibrium stages corresponding to about 150,000 individual extractions in 24 hours. The advantages claimed are the ability to determine purity of relatively complex and unstable systems as well as to obtain separation and allow quantitative determination of materials that are otherwise exceptionally difficult to analyze.

Significant applications of the technique have been made to the components of insulin (*111*); separation of phosphoric esters of biochemical importance (*218*); preparation of high potency oxytocic material (*171*); molecular weight determination of gramicidin S (*10*); separation of the natural estrogens, estrone, estriol, and estradiol-17β (*88*); and the elucidation of fat acid oxidation products (*306*). Perhaps the most significant results were those obtained in the study of several antibiotic polypeptides: gramicidin, tyrocidine, gramicidin S, and bacitracin. These results have been discussed and summarized by Craig, Gregory, and Barry (*68*). The countercurrent distribution method was shown to provide some unique checks on purity and homogeneity of complex materials of closely similar structure; in fact, to resolve systems that had not been separated adequately by chromatrographic methods, and were considered to be homogeneous. The study has also shown that the fundamental basis of countercurrent distribution, assumed by many to be closely similar to partition chromatography, is apparently different. The two methods serve as supplementary rather than competing approaches to separation and purification problems, and both may be profitably used in conjunction in the same study.

DETERMINATIVE PROCEDURES

ABSORPTIOMETRY

The absorption of radiation in the visible, infrared, and ultraviolet portion of the spectrum, and of x-ray was considered to be of the greatest value in a variety of determinative procedures (*139*), especially because it often is applicable without preliminary separation or treatment of biological systems. This previous emphasis on the value of absorptiometric method does not appear misplaced, even though it was difficult at the time of assessment to illustrate the applications of infrared absorptiometry in biochemical analysis; x-ray absorptiometry still has been little applied.

Visible Range. In the visible range, most applications of light absorption must be confined to measurement of colored materials formed as a result of adding appropriate reagents. This technique is approximately as old as quantitative biochemical analysis, but significant progress has been made within the past two years. Improved methods of measuring absorption or interpreting absorption data (*50*) have been developed; a new approach is the use of differential absorption to increase accuracy (*30*). The increasing utilization of multiplier phototubes (*207*) in spectrophotometry allows measurement of smaller light intensities and the increased use of capillary absorption cells (*281*). This combination has been developed (*71*) to provide submicrogram analysis of very small biological systems. A technique that promises to extend greatly the utility of both visible and ultraviolet absorptiometry is the subtractive method of Stearns (*261*), in which the contents of the blank absorption cell can be continuously altered by quantitative addition of the constituents of a mixed color system. The differential absorption of each component may be reduced individually until the relative absorption of the blank and the unknown compound over the entire wave-length range is matched, at which point the known composition of the blank is equal to that of the unknown. The utility of this technique is greatest when mixed absorbers show little difference in their absorption maxima. Several phases of analytical absorptiometry have been reviewed recently (*189*).

Infrared Radiation. Absorption of infrared radiation has perhaps developed more spectacularly than other phases of absorptiometry. Its wide employment in the petroleum industry for elucidating the structure of the difficult organic hydrocarbons made it possible to predict similar major contributions to the structure of biochemically interesting materials. No doubt this trend toward greater application of infrared absorption will continue, though it is now clear that some of the hopes for the technique are not realized in practice, while the equipment necessary is still scarce and expensive. Jones, Humphries, and Dobriner (*130*) tested the absorption spectra of 180 ketosteroids and steroid esters. They found the spectra to be characteristic of the type of carbonyl group and its position, thus clarifying to a significant extent some of the structure problems of these materials. The cis and trans configuration of peptide linkages was determined by Tsuboi (*276*), and Kuratani (*156*) demonstrated absorption bands due to carbonyl vibrations in amino acids and proteins. Kuratani's results could be explained only in terms of the "Zwitterion" structure of these substances. Infrared absorption by proteins is altered significantly by "denaturation" (*280*) but not by contraction of muscle proteins (*199*). Absorption by tissues has been shown to be characteristic of the individual organ; absorption by brain tissue, for example, is altered in insulin shock (*247*).

Polarized infrared absorption has been valuable in the elucidation of some features of desoxyribonucleic acid structure (*96*), in that the absorption indicated better agreement with Furberg's structure (*99*, *100*), derived from x-ray analysis, than with other proposed structures.

Blout and Fields (*26*) have shown that the infrared absorption provides an excellent method for identification and differentiation of seven common purines and pyrimidines and three methylated derivatives including caffeine, while Parke *et al.* (*210*) succeeded in quantitatively analyzing mixtures of acetylsalicylic acid, phenacetin, and caffeine in the presence of codeine salts and certain possible interfering compounds. The success of Thornton and Condon (*270*) in determining deuterium oxide over a range from 3 to 100% in water with a precision of 1% indicates the possible utility of the method in biochemical studies using deuterium.

Infrared absorption is perhaps more a means of studying structure than a true analytical tool, but its sensitivity to changes in certain definite absorbing groups indicates its value in detecting and determining these groups, enhanced by the fact that the sample may be measured intact and without destruction in the measuring process. This end is furthered by careful studies of quantitative application, such as those of Robinson (*232*).

Ultraviolet Radiation. Absorption of ultraviolet radiation has long been a valuable tool in the analysis for compounds having aromatic rings or conjugated double bond systems. The general extent of application of ultraviolet spectrophotometry to biochemical analysis has been indicated (*139*). General discussions of spectrophotometry over the visible and ultraviolet ranges are given by West (*287*) and Brode (*32*). A compilation of ultraviolet spectra of aromatic compounds is available (*97*).

Perhaps the greatest utility of ultraviolet spectrophotometry has been in identification and determination of nucleic acid components. It is a standard method for the determination of the phosphopyridine nucleotides which function as redox coenzymes—for example, see LePage (*163*). Rapid spectrophotometric measurements in the visible and ultraviolet are the basis of estimation of composition of catalase-peroxide intermediates according to Chance (*52*) and of reduced diphosphonucleotide–alcohol dehydrogenase protein by Theorell and Bonnichsen (*269*).

The ultraviolet absorption spectra of the pyrimidines and purines have been correlated with their intimate structure by Cavalieri and Bendish (*51*). Kunitz (*154*) has studied the kinetics of hydrolysis of desoxyribonucleic acid by desoxyribonuclease, measuring the optical density of acid-soluble nucleotides with ultraviolet wave lengths. A similar method may be employed for ribonuclease assay using ribonucleic acid as substrate. The photochemical breakdown of nucleic acid by ultraviolet irradiation has been studied in terms of ultraviolet absorption (*225*).

Ultraviolet absorption spectra of iodinated amino acids, iodocasein, and thyroglobulin have been determined (*184*). The photochemical breakdown of proteins and amino acids by continued irradiation with ultraviolet light was studied in terms of the change of absorption by McLean and Giese (*176, 177*). Hydrolysis of peptide bonds was found to increase ultraviolet extinction coefficients (*177, 239*). Constituents of cerebrospinal fluid have been investigated regarding ultraviolet absorption (*259, 266*), as ultraviolet spectrophotometry is suited to the determination of certain drugs, poisons, and abnormal constituents often determined in this fluid.

The important work of Caspersson (*48*) on the ultraviolet light absorption by components (chiefly nucleic acid and protein) of cells (*30*) has led to extensions of his general technique in similar studies of infrared absorption, fluorometric behavior, and specific combination of cell components with absorbing or fluorescent reagents (*190*). The microphotometer has been the indispensable instrument which can operate with the ordinary microscope, the quartz microscope, or the reflecting microscope in these studies. This subject is still comparatively new but may be expected to assume increasing importance as the techniques are developed.

The closely related field of noncellular fluorometry, long the analytical basis for determination of certain vitamins, should receive mention because it is beginning to provide analyses of other biochemical compounds. One such extension of likely importance is the determination of natural estrogens (*8, 9*).

TITRATION METHODS

While work of biochemical nature has not yet appeared using newly developed automatic titrators, it is evident that such titration equipment can serve in many routine analyses of chemical mixtures of biological origin. Careful fractionation procedures followed by semiautomatic analysis of individual fractions using a common reaction or property are certain to accelerate biochemical investigations.

Automatic analysis as applied to fractions separated by various chromatographic techniques has been accomplished using refractive index changes (*271*) and interferometry (*54*). Work is in progress with flow cell spectrophotometry (*58*) and coulometric titration to a pH end point (*78*).

Automatic instruments have been described for pH or potentiometric titrations (*7, 168, 220, 233, 289*) and for coulometric titrations (*169, 170*). At least three automatic pH titrators are available commercially in this country. The coulometric analysis procedures using electrolytic generation of reagent in the titration vessel (*89, 169, 170, 203, 223*) are unlikely to have widespread application in biological mixtures because of interference from electrolytic side reactions. The recent development of external generation of titrant ion by DeFord *et al.* (*79, 80*) eliminates indiscriminate electrolytic reactions, and greatly increases the versatility of such coulometric methods.

Automatic systems for the titration of volatile sulfur compounds by electrolytically generated bromine have been described (*6, 248*). The processes employed are examples of reagent generation *in situ*. DeFord, Johns, and Pitts (*77*) have developed an automatic coulometric titrator, using their previously described external generator (*80*). Electronic devices are employed to stabilize electrolysis currents and to terminate the titration at a given end point. For titration of an acid, the anode arm of the generator delivers sodium hydroxide at a constant rate, the equivalents delivered being calculable from the current-time relationships. The titrations are initiated by the operator but terminated automatically. Termination conditions may be chosen by the operator; in this case, the desired pH end point is chosen by setting a Beckman Model G pH meter. Presumably, amperometric end points, derivative polarographic end points (*230*), and perhaps high frequency end points (*1, 21–23, 110*) can be used in analogous fashion as terminators.

ISOTOPIC TRACER TECHNIQUES

Within the past two years, biochemical methods based on the use of isotopes have augmented rapidly. Isotopes are now well established as highly specific biochemical tools (*116*). The use of isotopes in analytical procedures is not increasing markedly, although isotopes may be used to define the best conditions of analytical techniques.

The chief value of isotopes, especially those of carbon, sulfur, and phosphorus, resides in their ability to distinguish between compounds already present and those compounds formed after supply of isotopes was initiated. For example, serine formed by enzyme systems from C^{14}-glycine may be identified as to origin by its isotopic carbon content, even in the presence of unlabeled serine of other origin. Thus the use of isotopes is increasing in studies designed to outline major pathways of metabolism in biological systems.

Greater discrimination in the use of isotopes is apparent, with increased availability of C^{14}-labeled intermediates. Thus, orotic acid is used to trace nucleic acid synthesis, as this compound is incorporated as uracil and cytosine in pentose nucleic acid (*4, 221, 227, 286*). This work may be contrasted with earlier work using the P^{32} isotope. The results from the work with phosphorus were less specific and conclusive, since the transformations which organic phosphates undergo in the cell are so numerous that complex fractionations are necessary.

In this regard, the recent use of *p*-iodophenylsulfonyl (pipsyl) derivatives to test purification schemes is interesting. The pipsyl chloride reagent may be synthesized containing either the iodine or sulfur isotope. The I^{127}-labeled pipsyl chloride may be used in preparation of derivatives from natural sources, while the S^{35}-labeled pipsyl chloride may be used in preparation of standard derivatives of expected compounds. Thus the fractionation of an unknown mixture containing one standard derivative should result in one fraction containing a constant ratio of radioactivity where iodine-labeled and sulfur-labeled pipsyl derivatives accompany each other (*278, 282*). In this way it is possible to identify a compound definitely, test its purity precisely, and apply the technique to quantitative determination.

Radioactivation by placing a sample in a neutron pile, later determining isotopes produced, is a sensitive method for detection of small amounts of elements present (*35, 200, 254*). However, this technique is available at present to a very limited number of biochemical analysts. The method has great potentialities for assessing the importance of biochemical trace constituents.

A new and possibly useful development is the increased utilization of tritium as a radioactive tracer for hydrogen (*15, 87*). General introduction to the use of tracers is provided by a number of monographs, that by Kamen (*132*) being the most recently revised. The large number of metabolic and pathway studies that have been performed by means of heavy or radioactive isotopes will not be discussed here.

The recurring theme in recent biochemical analyses has been upon carefully devised fractionation schemes coupled with rapid and reasonably accurate determinations using "family" properties or reactions. The trend has been less toward the development of new individual analyses or instruments and more toward the intelligent use of existing instruments.

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[End of Review Section]

Automatic Operations in Analytical Chemistry

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THIS year's review of progress in the automatization of chemical analysis follows the general form and content of the previous ones (*217*). As before, complete coverage of the literature is not intended. The references cited are actually only half of the total collected during the preparation of this paper. Those to be included were selected on the basis of representing significantly new developments or wider applications of previously described developments.

There seem still to be many cases where only part of the ideal of 100% automatization of a chemical analysis has been achieved. Thus the breakdown of analytical procedures into unit operations (ranging from obtaining the sample to recording the data), any one of which may be automatized, is continued as a logical method of classification. General trends and comments are first cited, followed by brief descriptions of specific automatic operations on the sample and on the desired constituent. As previously emphasized, the magnitudes of physical properties that can be measured electrically are those most useful in automatic analyses.

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GENERAL TRENDS

Sources of Information. The commercial literature continues to provide one of the most revealing sources of progress in this field. New instruments and applications frequently are announced first in this type of literature. While the claims made must often be taken with a "grain of salt" and basic theory may be described in fine print at the bottom of the page, much of this information appears to be factual and educational. Bulletins and trade journals should be used to the fullest extent by teachers and others interested in keeping up with the latest developments.

Only a few representative examples will be cited. Beckman

Instruments, Inc., has issued a descriptive bulletin (*26*) on the steps in producing instruments, which should lead to a greater understanding of the problems that must be met and solved by the instrument manufacturer. General Electric's folder (*99*) on laboratory products for chemical analysis contains ten pamphlets describing a variety of instruments. The "1950 Instruments Index" (*132*) represents the results of canvassing more than 1400 manufacturers during a 4-month period. It contains three sections: an alphabetical listing of products, a list of laboratory supply houses, and a directory of manufacturers, with complete addresses and brief descriptions of their products. Its usefulness would be enhanced if its columns were not chopped up into small sections with advertising in between.

The Minneapolis-Honeywell Co. has issued two bulletins of general interest, "Instruments Accelerate Research" (*182*) and "Fundamentals of Industrial Electrochemical Measurements and Automatic Control" (*193*). The Davis Instruments Division has made available a 19-page pamphlet (*77*) on "Methods and Instruments for the Continuous Analysis of Gases and Vapors" which includes three categories: calorimetry (catalytic combustion), thermoconductometry, and electroconductometry.

The use of motion pictures is also encouraging and recent announcements have been made of the availability of instrumentation color films by the Eastman Kodak Co., and the Taylor Instrument Cos.

Academic Trends. There seems to be an increasing concern over the lack of emphasis on the fundamental physical principles on which modern instruments are based. Müller has stated (*199*) that "education in instrumentation is so far behind the current trend that it is already a serious bottleneck."

The training of the modern analytical chemist, either in industry or in educational institutions, will be more rewarding if he is taught more than merely which button to push, and when. An understanding of what is being measured, as well as its relation to the particular chemical concentration being sought, is often vital. For example, Silsbee's paper (*249*) on standards for electrical measurement and the calibration program at the National Bureau of Standards cites the importance of precise electrical measurements to modern science and industry. Terry (*267*) describes the basic principles used in measuring and controlling instruments and gives examples of each.

More and more training seminars and short courses are being established. For example, the Minneapolis-Honeywell Co. in 1951 organized its first "formalized get-together" for staffs of colleges and technical schools. At least three schools have organized short courses: Massachusetts Institute of Technology, Texas Agricultural and Mechanical College, and University of Florida.

Several papers emphasize the importance of training with modern instruments for analytical chemists (*209*, *237*, *239*). Murphy, especially, reiterates that the student must learn the fundamentals of instrumentation rather than the mere operation of equipment. Rosenblum (*237*), however, cautions that the industrial analytical chemist should not be required to be an instrumentation expert or even to perform the measurement personally, but that he should clearly understand the potentialities of the various methods of measurement.

The meaning of the term instrumentation itself continues to be defined and redefined, used and misused. The opinions (*32*) expressed by Klopsteg and by Behar concerning the use of the words "instrumentation" and "instrumentology" indicate the differences in interpretation which may exist. It seems almost superfluous to state that instrumentation has, by the very fact of its increased usage in all fields of science, become a general inclusive term, rather than one indicating any one specific meaning.

The emergence of instrumentation as a field of science in itself has been further supported by Behar in his opening chapter in "The Handbook of Measurement and Control" (*31*). Entitled "Classifications—Keys to Know-How," it features a number of original definitions and ideas on the scope of instrumentation, as well as its problems and applications.

Condon (*69*) has raised the question, "Is There a Science of Instrumentation?" and discusses generally the various aspects of measurement, now coming into its own as a separate science. He classifies properties into discrete and continuous, and proposes a number of clarifying definitions. Wildhack has also discussed the field in his paper "Instrumentation in Perspective" (*284*).

A number of recent statistics indicate tremendous growth in the field of modern instruments. One of these is a tabulation (*231*) of new instrument items reported in *Instruments* each year since 1928. Substantially constant at about 650 during the postwar years 1946–48, the number jumped to 798 in 1949 and to 1063 in 1950. While not all of these were of direct interest to the analytical chemist, many were. Figures released by the Scientific Apparatus Makers Association (*243*) reported industrial and laboratory instrument sales up 45% for the first half of 1951, compared to the corresponding period in 1950.

General Reviews in the Literature. A number of review papers concerned with instruments in automatic analysis have appeared during the past year. Lassieur (*155*) treats the subject from a historical viewpoint, while Marchment (*176*) points out the impetus which electronics has given to measurement and process control.

Thomas has published reviews (*134*, *270*, *271*) on continuous analyzers with comments on the operating principles of infrared analyzers, densitometers, dielectric constant meters, and refractometers. He particularly stressed developments in the past 3 to 5 years toward simplifying analytical work by eliminating the need for submitting process samples to laboratories by placing the new analytical tools directly in plant control rooms. For every dollar spent on continuous analysis instruments, a return of about $3.00 per year thereafter is realized. He further comments on the difficulties resulting from the secrecy so often encountered in discussions where actual process variables may be important. The need for more cooperation with instrument manufacturers is evident. Thomas concludes with the statement, "the surface has only been scratched."

The advantages to be gained are well exemplified (*215*) in the solving of an infrared analysis problem by cooperative contributions from Baird Associates, Du Pont Experimental Station, Esso Development Co., Mellon Institute, and Gulf Research Corp. The problem involved was the determination of ethylene in the presence of ethane and methane.

Other general papers include Adeszko's "One Knob Production Control" (*2*) and Evans and Holzbock's "Remote Supervision of Industrial Production Processes" (*93*). The "Handbook of Measurement and Control" edited by Behar (*31*) has two chapters of interest to analysts, Chaplin's "Instrumentation for Chemical Analysis and Control" and Peterson's "Instrumentation in Research."

Two reviews on methods of determining water in air or other gases have also appeared. Riesenfeld and Frazier (*230*) conclude that there now is no suitable automatic method for measuring the water dew point of hydrocarbon gases. Mabey (*171*) feels that "it is curious that as familiar a physical phenomenon as the presence of moisture in the atmosphere still lacks a generally satisfactory method of precise measurement."

Cook (*70*) has stated that air analysis by continuous-recording devices is the principal means of evaluating the exposure of persons to injurious materials. He mentions recording devices for flammable vapors, carbon disulfide, hydrogen sulfide, carbon monoxide, ionizing gases, and nuclear radiation. Hartwell in a pamphlet on "methanometry" (*120*) discusses various devices for measuring methane concentrations.

Significant usage of statistical studies has been reported in at least two papers. One (*282*) reports 95% confidence limits for an automatic potentiometric titrator, while the other (*281*) describes the use of statistics in evaluating the precision of various

types of electrical instruments for determining moisture in textiles. Analysis of variance and designed experiments were used for comparison purposes.

Meetings. An increasing number of meetings of various nonchemical organizations merit more than passing interest. The Instrument Society of America held its Sixth Annual National Instrument Conference in September 1951, which featured the largest exhibit of instruments ever held in the western hemisphere (*63*, *135*). The Scientific Apparatus Makers Association held meetings in September and October 1950 (*58*) and in April 1951 (*6*). Upward trends in the production of scientific instruments, as well as increased standardization efforts, were evident. Müller (*199*) made a strong plea for an industry-wide conference on automatic analysis and considers the wider use of automatic measurements as vital to the success of America's defense efforts. The question and answer session, which followed papers presented at the Texas Agricultural and Mechanical College Symposium on Instrumentation for the Process Industries, has been published (*134*) and provides a very clear glimpse of the present-day problems in automatic analysis.

Reports on Europe's industrial and instruments fairs indicate accelerated activity there also. Rimbach (*232*) has reported on exhibitions in England, France, and Germany. Mayor (*177*) has reviewed at some length the exhibition at Frankfort, Germany, held in July 1950. A special issue of *Chimie analytique* (*64*) describes many automatic instruments at the Paris Exposition in November 1950. It includes a list of European manufacturers and their addresses and products, as well as a number of literature reviews, covering European developments in the automatization of analytical chemistry.

Design of Automatic Instruments. Although the analyst may not be expected to participate in the actual design of his instruments, he may frequently be concerned with the details of construction, especially when things go wrong. Space prevents more than a superficial glance at some of the more outstanding trends in design. The cartoons in Figure 1 humorously emphasize two divergent trends in present-day instrument design: versatility and simplicity. While many analysts would like to have a device that would do everything, such factors as cost (initial and upkeep) and portability continually force compromises on the designer. Munch (*208*) points out that the remarkable performance characteristics of some instruments are achieved by making the instrument more complex, resulting in higher costs. While many applications justify the extra expense, Munch feels that some situations can be solved inexpensively rather than by the usual costly complex instruments. An extreme in the trend toward simplicity of operation may be cited in an advertisement (*68*) of a new alternating current pH meter which features "no buttons to push."

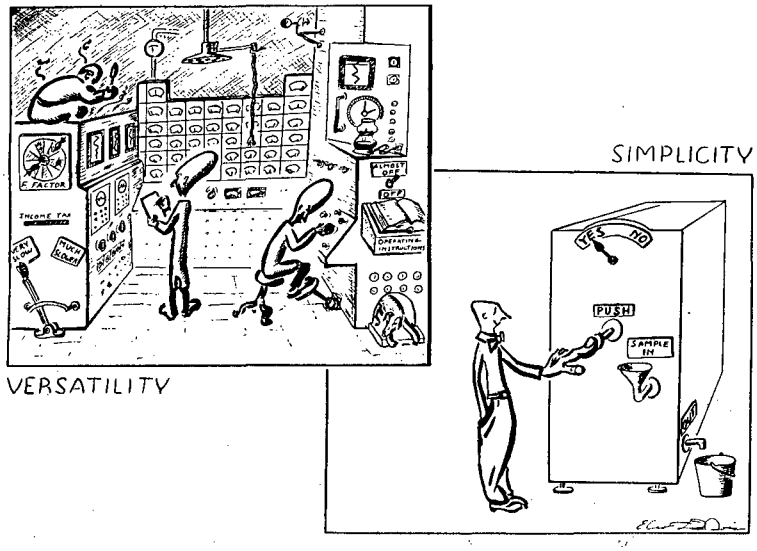

Figure 1. Automatic Instrument Design
Reprinted from "Better Analysis" by permission of Baird Associates, Inc.

Two other trends are evident in the literature concerned with instrument design. One is an increasing awareness of the importance of electronics, and the other is the increasing availability of component parts which may be bought separately by the user and assembled as he sees fit.

Aronson has begun a very elementary series of articles on "instrument electronics" (*13*), which starts with a consideration of the electrical nature of matter and then describes the basic circuit elements, resistors, capacitors, and inductors. Slater (*251*) reviewed vacuum-tube instrumentation for the measurement of variables in the food industries.

Clark (*66*) contends that electronic circuits for instruments require components of higher quality than are used in radio work. He emphasizes that price is not nearly so critical as such factors as long life, dependability, ruggedness, stability, and low noise level. A reading of Clark's paper creates a greater appreciation of the fallibilities of the components of instruments on which the analyst so readily depends. Clark surveys recent developments in resistors, transformers, capacitors, printed circuits, switches, and vacuum tubes. Marchment (*176*) also has reviewed developments in electronic instrumentation and included a note on safety precautions, especially means of preventing sparks which might cause explosions. Glansholm and Kleman (*102*) review the use of photomultipliers in spectroscopy, with a summary of the characteristics of commercially available nine-stage tubes.

Gutmann (*111*) has written a lengthy review on electronic instrumentation for chemical laboratories. His formal training was in physics and he had subsequent experience in the design and development of electronic equipment. His paper, addressed to radio engineers in Australia, represents an interesting attempt to acquaint such a group with the uses that electronic techniques have found outside the realm of communications. In this way it fulfills Müller's suggestion (*199*) that analysts should "brief" instrument specialists on their specific requirements, leaving the ultimate solution in their hands. Gutmann discusses pH meters, current amplifiers, colorimeters, polarographs (including a new method where an alternating current potential is superimposed on the usual direct current potential), gas analyzers, potentiometers, electrolytic conductance bridges, dielectric constant meters, moisture meters, supersonic apparatus, electronic control apparatus, radiometric devices, and miscellaneous electronic aids (including electronic balances). He cites 96 references, includes 25 figures, and frequently mentions areas in which further development is needed.

A number of items in the trend toward greater availability of instrument components deserve mention. One trade journal (*219*) points out that there are three steps in the evolution of a new instrument: a recognition of the need, construction of the prototype, and evaluation of its merits. The availability of component parts or "building blocks," which may be assembled in different combinations, should help eliminate delays in the second step. Examples include such items as monochromators, amplifiers, detectors of various types, null-balance measuring devices, magnetic memories, and bridges (*3*, *47*, *53*, *59*, *94*, *219*, *263*). Even such small items as indicator lights, fuseholders, chassis, and plug-in kits may be extremely useful when constructing or altering instruments (*3*).

Frommer (*97*) has described a new measuring and proportioning method which may be applied to the measurement of photocurrent, ionization

current, or the like. Essentially the arrangement provides for automatic continuous calibration, in which the detector—e.g., a phototube—is exposed to the varying phenomenon continuously and to a constant phenomenon periodically. Thus the current obtained represents the measured magnitude in one period of the cycle and the sum of the measured and standard magnitudes in the other period. A novel circuit is then described which makes use of the facts that (*a*) the logarithm of the ratio of the two currents is the difference between the logarithms of each, and (*b*) circuit elements are available, the voltage across which is a logarithmic function of the current flowing through them.

Washburn *et al.* (*277*) have discussed factors in mass spectrometer design, including temperature control and mechanical stability.

THE SAMPLE

Continued activity in the development of improved sampling devices is evidenced by the number of devices designed primarily to perform operations on the sample. Special emphasis has been placed on solving problems of obtaining truly representative samples. Both gases and liquids, in spite of their free-flowing characteristics, frequently present serious sampling problems.

Three patents for gas sampling have been issued which are of interest to automatists. Austin's device (*17*) was designed to take a gas sample that is directly proportional to the flow rate of a flowing gas. Hall (*115*) described a gas-sampling apparatus for hydrocarbons which was designed to give a weighted gas sample, collected over a period of time, depending on the rate of flow of the gas. McEvoy's apparatus (*174*) was designed especially for flowing combustion gases.

Smith (*253*) has published a review of the fundamentals of atmospheric sampling. Brown *et al.* (*48*) have described a new apparatus for the partitioning of expired air in respiratory studies. It partitions each expired breath into seven fractions and has been useful in the study of lung retention of inhaled particulate matter.

Recent announcements of commercial gas samplers include the use of the Cartesian manostat (*109*) in carbon monoxide analyzers where the air flow is maintained at a constant optimum rate, designed to provide maximum sensitivity and stability. Automatic sampling arrangements for carbon dioxide and oxygen recorders have also been announced, one based on trapping a definite volume (*125*), and the other based on a special differential-pressure aspirator (*126*) which gives a constant flow of gas sample regardless of changes in the suction or flow of the main gas line. Another (*226*) measures sampling rate of a recording gravitometer using a float-type flowmeter. An automatic compensator takes care of changing atmospheric conditions.

A large number of liquid samplers have been designed to collect effluents from various types of columns. Much of the tediousness of collecting separate fractions from chromatographic columns has been relieved by such devices (*88, 101, 106, 119*). All are actuated electronically, and the main differences are in the switching arrangements, which may be actuated by the weight of the sample operating a solenoid or a mercury switch, by an electronic capacity switch, or by a photoelectric unit combined with solenoid valves. A commercially available chromatographic fraction collector for up to 200 samples, which may include a photoelectric drop counter, has also been announced (*265*). An automatic fraction collector has been described for use with vacuum distillations (*250*).

A water-wheel type of liquid sampler has been designed for sewage (*229*). Another (*113, 114*) is based on a ring balance meter and allows a choice between two types of intermittent sampling systems and three types of continuous sampling systems. Hauck (*122*) points out that difficulties frequently arise from the fact that both the composition and flow rate of the waste stream are likely to vary considerably. Also, different specific gravities complicate the sampling problem: Oils concentrate near the surface, while inorganic precipitates settle out at the bottom. He gives a thorough discussion of the location of the sampling point(s), automatic collectors (with a warning that composite samples may be misleading), the preservation of sample properties, and flow measurement.

Reinke and Herscher (*227*) describe an automatic cell changer for single-beam spectrophotometers where the cell slide is moved back and forth, to place the blank and the sample in the radiant-energy beam for timed intervals. Thus, a synchronous motor cam arrangement enables the recorder to plot the I_0, I, and zero lines one above the other on the same chart. A commercial motorized automatic pipet has been described (*254*), primarily for biological use, in models which can make up to 95 deliveries per minute of volumes between 0.1 and 10.0 ml. An automatic sample changer for windowless gas flow radioactivity counters has been developed by Nye and Teresi (*212*). The instrument records the time in seconds and automatically changes the sample after a predetermined number of counts.

The only major activity for automatic treatment of samples has been in the field of combustion. Cannon (*54*) designed a moving Tirrill burner for use in micro-Dumas analyses, while a commercial high-temperature microcombustion furnace (*269*) has been made available for direct determination of oxygen in organic compounds by the Unterzaucher method. Millen and Vrendenburg (*179*) described the use of an induction furnace for carbon in steel, with automatic timing and oxygen introduction.

THE DESIRED CONSTITUENT

Separation. Whenever the desired measurement cannot be made directly on the sample, automatic means may be used to separate the desired constituent in a form which may be measured. The classical method of analytical separation, precipitation, has not been automatized, but many other types of separations lend themselves readily to mechanization. One of the few general papers on automatic separations is Smith's review (*253*) of fundamental methods of atmospheric sampling, including electrical precipitation, thermal precipitation, impingement, mechanical filtration, absorption, adsorption, and the use of freeze-out traps.

One of the most promising methods for automatic separation of liquids is volatilization, and a number of papers have described new automatic distilling devices. Dixon and Ronnebeck (*85*) have described an automatic laboratory still for high-efficiency batch fractionations. Highet (*129*) designed one for continuous operation in which constant rates of flow of feed and distillate are maintained. Peppard (*218*) developed an electronic timer-controller in conjunction with a magnetically operated still head to operate the valve and to control the reflux ratio.

Several commercial units have been announced. Podbielniak, Inc. (*222*), offers semiautomatic laboratory analyzers for high-temperature distillations ($-40°$ to $+350°$ C.), as well as an automatic model for low-temperature distillations ($-200°$ to $+100°$ C.). Both types feature strip-chart recording potentiometers. The Precision Scientific Co. (*223*) offers an automatic distillation apparatus specifically for use with various ASTM tests. It records volume and temperature continuously and was designed by Rolfson *et al.* at the Shell Development Co.

Two automatic stills for purification purposes have been described, one for water (*72*) and the other for mercury (*55*).

Distillations actually include condensation as well as volatilization as separation steps. There are some situations, however, where the sample is originally in the gaseous or vapor state, and condensation may be the only operation required for separation. Examples include such equipment as dew point devices (*98, 131, 171*) and automatic frost point hygrometers (*145*), where the water condenses onto a shiny surface, thereby reducing the reflectance of a light beam incident upon it.

A volatilization method other than distillation consists of a

degassing unit for steam sampling (*234*). Its purpose is to eliminate interference from carbon dioxide and ammonia in electroconductivity methods for steam purity. It provides two streams of condensate, one containing all solid impurities and the other containing all gaseous impurities of the original sample. The gases are removed by passing the condensate through reboil coils, where gases are eliminated and the water recondenses at the boiling point. The commercial version of this apparatus (*113*) has a very small lag time.

Another very promising means of separation is sorption. A number of investigators report progress in their work on paper and columnar chromatography (*202, 203, 286*). Adsorption of hydrocarbon gases followed by elution by air or by heating may be a useful technique (*50, 274*). A commercial apparatus (*50*) is available for separating, measuring, and collecting the components of light hydrocarbon gas mixtures, based on adsorption fractionation.

Automatic separations based on absorption have been described for removal of carbon monoxide or carbon dioxide (*33, 45, 285*).

Four papers have appeared in the past year which describe automatic separations by liquid-liquid extraction. Morrison (*197*), in his review of the role of extraction in analytical chemistry, describes the increasing use of continuous extraction methods. Cohen (*67*) has designed a very simple low vacuum apparatus for the removal of steroids from urine at low temperatures. Stepanov *et al.* (*257*) have designed a laboratory countercurrent extractor. Craig and his coworkers (*73*) have described a discontinuous extraction train which can perform about 150,000 extractions in 24 hours.

Electroseparations of various types have been automatized and recent developments include Lamphere's (*153*) wide range (up to 100 volts) instrument for controlled potential electrolysis, Vollrath's patent (*275*) on an electrical precipitator to clean gases being sampled, and a simple process (*107*) for continuous separation of mixtures on filter paper by electrophoresis. In the latter apparatus, a continuous flow of the liquid sample passes downward through a vertical sheet of filter paper. At the middle of the paper the two electrodes are located, and the resulting electrophoresis causes the components of the solution to spread sidewise as the flow downward progresses. They can be collected at the bottom of the paper sheet in separate containers. The process has been applied to various protein and amino acid mixtures.

Magnetic methods of separation as used in mass spectrometry have been found very useful for continuous analysis. Robinson *et al.* (*207, 235*) developed a mass spectrometer for monitoring continuous processes, while Miller *et al.* (*180*) used a mobile mass spectrometer to provide a continuous record of the nitrogen content of alveolar expiration gases. Starr (*62*) reported applications of the leak-detector type of mass spectrometer to the continuous monitoring of single components and of a specially constructed instrument for multicomponent gas analysis.

Miscellaneous automatic methods of separation include diffusion (liquid and gaseous), thermal precipitation, centrifugation, and dissolution. The liquid thermal diffusion technique (*144*) has been applied to the continuous separation of long-chain molecules. It is useful in separating components in cases where no differences in mass exist. Gaseous diffusion of hydrogen through palladium has been used in a thermoconductometric method for the determination of oxygen in organic compounds (*118*). Bredl and Grieve (*43*) designed a thermal precipitator for use in the separation of solid particles in flue gases. The Dietert Co. (*82*) has announced a microparticle classifier which separates particles in the 0- to 60-micron range into eight fractions. The dissolution method of separation is used in an automatic mercury washer described by Bergmeyer (*35*).

Gravimetry. Duval and 14 collaborators (*61, 89*) have described the use of continuous weighing for analytical purposes and have summarized their thermobalance work during the past five years. The use of the automatic thermobalance seems to be spreading, except in the United States. Borrel and Pâris (*41*) reported thermogravimetric studies on metallic compounds of 8-quinolinol, while DeCarli and Collari (*79*) made a thermogravimetric study of the oxidation of metals, and Shiokawa (*247*) applied the technique to the analysis of rare compounds with tungstosilicic acid.

There have been few commercial developments toward the goal of the fully automatic balance which would print the weight, as well as indicate it directly, during the past year. A new series of "metrogram" balances has been put on the market (*154*), which features electronic indication of the null point. However, the best sensitivity on these models is 10 mg. where the capacity is 2 kg.

Perhaps more promising is the use of a strain gage load cell in an electronic weighing system (*260*). Although designed for heavy industrial loads, the principle would seem adaptable to analytical weighing as well. In its present form the best available "readability" is 1 pound. The load cell is located in one branch of a bridge circuit and consists of a variable-resistance strain gage bonded to a machined load member. When the load member is strained, the resulting voltage change in the strain gage causes bridge unbalance, and this actuates a motor which adjusts a compensating variable resistance. The motor also positions a step cam printer to locate the correct type of wheel positions for printing the weight on a ticker tape or a ledger sheet.

Lohmann (*168*) has described an electronic recording analytical balance which plots a continuous record of changes in weight with respect to time. The recorder is free of all mechanical connections with the balance beam. The sensitivity of the balance can be varied by a knob control, and slow or fast rates of changes of weight can be recorded. Although designed for use in physical studies of the mechanics of impregnated resins which change weight because of volatilization, this balance could follow rates of sorption, desorption, evaporation, oxidation, and decomposition. Balance displacement is detected by a light source–phototube arrangement, and a servomechanism operates the gear-driven chain for keeping the balance at equilibrium.

A French patent (*285*) describes an apparatus for continuous analysis of carbon dioxide, which passes the gas through a vessel containing a constant volume of a liquid (sodium hydroxide solution) which is being continuously renewed. The vessel is supported on a balance which indicates an increase in weight when carbon dioxide is absorbed.

Volumetry. Volume measurements on gases, liquids, or solids continue to be useful for various kinds of analytical automatons. Lilly (*166*) has described a new type of nitrogen meter which records nitrogen gas and inspired and expired volumes of a person's breath. The total volume of the inspired and expired gas is measured by having the subject breath into and out of a large rigid reservoir. The volume changes cause pressure changes and these are recorded to give a fairly linear record at ambient temperature and pressure. The nitrogen is measured by a new nitrogen meter based on radiant-energy emission (described under Emissimetry).

The Hays Corp. (*125*) markets a new recorder based on the Orsat principle. The volume of the sample is measured before and after absorption of the carbon dioxide. Each cycle takes about 2 minutes. The apparatus is water-powered and can be taken apart with only a screw driver and a small wrench.

Volumes of liquids may be measured by a new automatic pipetting machine (*5*), or by a dual-purpose "titrometer" and dispenser (*96*) consisting of a modified electric record player, and an electrically controlled pressure regulator to maintain a constant flow of reagent. A vacuum-operated "automatic" buret (*38*) has been described. Actually, this is typical of so-called automatic burets which are not fully automatic—the operator still must operate the stopcock and read the meniscus.

Godfrey *et al.* (*104*) designed an automatic biological assay apparatus in which a new type of valve was used to supply and drain solutions to and from an isolated organ bath. The assay of *d*-tubocurarine, for which it was designed, involves emptying and filling an isolated organ bath nearly 100 times at precise intervals, and accuracy demands that the bath be filled to the same mark each time.

Volumetric measurement of solids continues to be an important means of determining relative humidity. Mabey's review (*171*) describes hygroscopic hygrometers which depend on changes in physical dimensions of cellular organic materials. One commercial humidity indicator (*1*) contains a sensing element of 216 inches of fine blond human hair.

An apparatus for the introduction of solid reagents (*9*) consists of a motor-operated device for introducing a solid charge at a slow, constant rate into a tube furnace over periods up to 8 hours. A solenoid-operated vibrator prevents sticking.

Densimetry. Relatively few new developments have been reported in the field of measuring density and specific gravity. Thomas' review of continuous analyzers (*271*) includes a survey of the current status of the field. Accuracies of two units in the fifth decimal are obtainable, and numerous applications have been made of various commercially available instruments. Two companies have recently announced densimeters for gases (*226*) and for liquids (*224*), both based on the float principle.

Manometry. Jacobs (*136*) has described an ingenious use of automatic measurement of pressure for continuous vapor-pressure control of petroleum products, which eliminates the usual 4-hour delay formerly necessary in the use of the standard Reid test.

Manometric measurement is the basis of two carbon dioxide–measuring devices. Bennett (*33*) described one for carbon dioxide in flue gases which consisted of a pneumatic bridge circuit with an absorption vessel in one arm. The pressure differential between the mid-points of the two limbs of the circuit is a direct measure of the amount of carbon dioxide removed. The other apparatus (*233*) was especially designed for carbon dioxide in anesthetic gases. Two porous unglazed cylinders, one of which contained soda lime, were connected to a manometer, so that the pressure differential measured the carbon dioxide present. The apparatus worked satisfactorily in the presence of nitrous oxide, oxygen, diethyl ether, chloroform, trichloroethylene, or cyclopropane.

Several new types of recording or indicating manometers have been reported. Greenough and Williams (*108*) designed an electronic circuit for measuring the displacement of pressure-sensitive diaphragms, based on a mutual inductance micrometer. It gave full-scale deflections for motions of less than 5×10^{-4} inch. Lilly's instrument (*166*) for measuring inspired and expired breath has the subject breathe into and out of a large rigid reservoir; pressure changes are continuously measured by a rapid electric condenser pressure gage. Redfern (*225*) described an electrical recording pressuremeter for measuring the gas pressure produced during fermentation in a sealed vessel. Up to 12 separate pressures could be recorded simultaneously on a strip chart recorder. Dibeler and Cordero (*81*) designed a diaphragm-type micromanometer for use on a mass spectrometer that measures pressures of 1 to 100 microns. A sensitivity of about 0.1 micron was achieved by eliminating mechanical coupling between the specially designed diaphragm and the displacement-measuring device. Displacement was measured by the change in mutual inductance of two fixed concentrically wound coils mounted above the center of the diaphragm. Bristol Co. (*46*) has described the measuring elements of pressure recorders.

Berg (*34*) has described an apparatus for measuring the carbon dioxide or water vapor evolved from mineral samples at various temperatures by means of a differential manometer. The Dwyer Co. (*90*) has announced a portable carbon dioxide indicator consisting of a pressure gage with a pointer dial reading directly in percentage of carbon dioxide.

Viscometry. Few truly new advances in this field have been evident during the past year. Kilpatrick (*146*) has patented a continuous-reading viscometer for use in hydrocarbon-processing operations. Like many other modern viscometers, it measures resistance to torque. Thickens (*268*) has described a capacitance-change viscometer, which is a modified Wagner cup-and-ball viscometer in which the spacing between the cup and the ball is measured by a capacitance method with a variable-frequency oscillator. It is applicable for measuring the relative viscosity of nonconducting liquids.

Magnetometry. The magnetic susceptibility of oxygen continues to be a popular method for its determination, but there have been no significant improvements or changes in the technique used. Medlock (*178*) has reviewed oxygen analyzers based on its paramagnetic properties, with details on an improved type of instrument using the "magnetic wind" principle. Gases having high thermal conductivities interfere. Kundt (*152*) has discussed the thermomagnetism of oxygen and its use in gas analysis. Two companies (*25*, *126*) have issued new descriptive bulletins on the subject.

Thermometry. Measurement of temperature has been the basis of a number of automatic methods. Ilfeld (*131*) has described the General Electric dew point recorder (*98*) in detail, with emphasis on its applications and limitations. Jury and Licht (*145*) developed an automatic frost point hygrometer where the water vapor frosts out on a gold surface which is cooled to as low as −90° F. It was designed to determine very small amounts of moisture in air, with applications to air conditioning, food processing, and the control of noncondensable inert atmospheres. A light beam–photocell heater arrangement is set to maintain a predetermined thickness of frost on the surface, so that the frost point is indicated continuously by a thermocouple potentiometer.

Automatic freezing point and boiling point devices have been described (*128*) in which the temperature-sensitive elements are thermistors. Temperature differences of 0.001° can be measured over the range −40° to +140° C.

Two papers describe apparatus for thermal analysis. McConnell and Earley (*173*) used Leeds & Northrup control and recording equipment (*183*) in an arrangement giving satisfactory performance up to 1100° at a heating rate of 10° per minute. Jellinghaus (*141*) critically reviewed the usual methods for thermal analysis and described a device which permits automatic recording at a heating velocity of about 1° per minute.

Calorimetry. The heat liberated upon the catalytic combustion of combustible vapors continues to serve increasingly as an automatic indication of the explosives content of gases. Hartwell's review (*120*) of "methanometry" describes various contemporary instruments based on this principle.

Turkeltaub's elaborate gas analyzer (*274*) measures total hydrocarbon content in one part of a gas stream by combustion on a platinum wire. The other part of the gas stream passes over carbon, which removes the hydrocarbons. Stepwise elution by air then follows, and the subsequent combustions on the platinum wire provide calorimetric measurements of the separate fractions.

New commercial devices have been made available during the past year for carbon monoxide (*109*), various explosive gases (*16*, *75*), and oxygen in the range 0.0002 to 0.0200% (*20*), as well as a "sniffer" for combustible gases in marine applications (*143*).

Davis (*77*) has announced a new design which circumvents the difficulties with zero drift, inherent in most calorimetric devices dependent on catalytic combustion on a platinum wire. The trouble arises from the fact that the temperature increase has traditionally been measured by the change in electrical resistance of the wire when it heats up. As the wire ages with use, metal evaporates slowly and its resistance thus increases because of the decreased cross-sectional area, causing a zero drift in the instrument. The new apparatus (*77*, *78*) avoids this trouble by

measuring the temperature change with a thermocouple. Several models are available: a single-point recording remote head unit, and a tube sampling indicating or recording analyzer for sampling from three, four, six, or eight different locations or areas. The single-point unit is useful for supervising ovens driving off combustible vapors or solvent recovery systems. On the multipoint sampling analyzer, the touring cycle of the system allows a time dwell at each point for about 30 seconds.

Titrimetry. The potentialities of automatic titrators are well indicated by the number of papers on the subject which have appeared during the past year. Hawes, Strickler, and Petterson (*124*) have described the Beckman instrument (*29*), giving the design requirement together with sketches, photographs, and circuit diagrams and details of the special anticipation circuit which causes diminishing stepwise addition of the titrant as the end point is approached. The Precision-Dow recording titrator has been newly described also, as well as continuous titration with controlled-volume pumps (*190*).

Dunn *et al.* (*87*) have described a dual automatic potentiometric titrator with greatest utility for titrations in nonaqueous solvents for mercaptan, sulfide, and salt determination in petroleum or petroleum products. Jacobsen and Léonis (*137*) constructed an inexpensive, direct-reading titrator of the Lingane design, using a pH meter. They found it useful for controlling the addition of acid or base to a liquid system to maintain constant acidity during reactions in which hydrogen ions are produced or consumed. Fowler *et al.* (*96*) designed a dual-purpose titrator and dispenser consisting of a modified electric record player which serves as a timer, an electrically controlled pressure regulator to maintain a constant flow of reagent, and a galvanometer connected to two half-cells to indicate the end point of a titration. With this apparatus 200 assay tubes were titrated in 120 minutes.

Jenšovský (*142*) designed an automatic titrating device using a sensitive electromagnetic relay to turn the spring-operated stopcock off. He found platinum and graphite electrodes most suitable for oxidimetric titrations and platinum and pyrolusite for reductimetric titrations. Widing and Farquharson (*282*) tested an automatic potentiometric titrator statistically by calculating 95% confidence limits. They followed the general designs of Lingane and of Robinson and reported good results in the determination of uranium with ceric sulfate. DeFord *et al.* (*80*) have devised an apparatus for automatic coulometric titrations with externally generated reagents, which has the advantage of requiring no standard solutions. The constant current used for generation of hydrogen or hydroxyl ions was uniquely regulated by using a by-pass type of regulator not requiring the load current to pass through the control tube, thus allowing generation currents above 100 ma.

Müller (*201*) has urged a re-examination of the usefulness of photometric techniques for autotitrators, as well as the larger question of the proper role of an autotitrator. He seems convinced that colorimetric end-point detection should be better than electrometric detection. Others have noted the problems of lag due to inefficient stirring and delays in attaining electrode-solution equilibrium. Nichols and Kindt (*210*) have described a photoelectric titrator, using two barrier-layer photocells, which has a high differential sensitivity. They suggest several improvements, such as a line voltage stabilizer, the use of narrow-band filters, and a better bridge circuit.

Shell Development exhibited (*63*) a new continuous recording electrometric titrator at the Instrument Society of America exhibit at Houston. It was designed for determining mercaptan concentrations in gasoline, but is applicable to other electrometric problems.

Emissimetry. Direct-reading spectrometers, measuring emission-line intensities by photoelectric means, have found wide acceptance. Over 50 production control quantometers have been installed (*11*) and the latest model permits analysis of as many as 20 elements simultaneously. One general paper (*121*), as well as others describing its use for aluminum (*52*, *65*) or brass (*272*), has appeared.

Progress in Europe on direct-reading spectrometers has been reported by three authors. New instruments have been described (*42*, *117*, *273*), with applications to the determination of phosphorus and carbon in steel (*42*) and of various metals in steel and zinc (*117*). A new instrument is being developed in France (*4*) which uses only two photoelectric cells to study the whole spectrum of a metal. One standard cell is stationary, while the other cell is motor-driven along the spectrum.

Although less spectacular, a few new developments have been reported in accessory equipment for ordinary photographic spectrographs, including two recording densitometers (*139*, *252*), and an electronic regulator (*169*) of excitation and exposure of spectra, which operates the switches, the shutter, and the plate holder.

Advances (*147*, *244*) in the instrumentation of flame photometry methods have raised the question of the possibility of the continuous determination of such metals as calcium and magnesium (*242*). A portable halogen analyzer has been recently commercialized (*76*) which employs a photoelectric photometer to indicate changes in the intensity of the blue spectrum of a copper arc discharge when organic halide vapors are present. It covers a concentration range of 0 to 500 p.p.m. with an accuracy of 10%.

Emissimetric methods for determining gases have been the subject of some study. High-frequency excitation with external electrodes can be used for quantitative spectroscopic analysis of mixtures of nitrogen and carbon dioxide with oxygen (*283*). Lilly's nitrogen meter (*166*) for respiration studies measures the nitrogen at the subject's mouth. The breath is sampled by an orifice-vacuum system which carries the air through an electrical discharge tube. The radiant energy emitted by the flowing sample passes through appropriate filters and then to photocells. The apparatus will record a change from 0 to 80% nitrogen in 0.02 second.

Infrared Absorption Methods. Thomas (*134*, *271*) has described the use of infrared radiant energy in his review of continuous analyzers. The newest nondispersion infrared analyzers may use any part of the region from 0 to 14 microns. Thomas describes applications and lists five manufacturers from whom infrared analyzers may be purchased.

Baird Associates (*19*) have announced a redesigned recording gas analyzer which is compact, easy to service, and suited to adverse plant conditions. Based on the subtractive (Luft) filtering principle, it has a double beam and two bolometer-detectors. Hartz (*63*) described an improved Luft-type infrared analyzer made by the Mine Safety Appliances Co. It is also double beam but has only one detector (the beam is alternately sent through the two stainless steel gas-sample cells by a reciprocating metal slider), so that zero shift is minimized. The detector is of the condenser-microphone type. The instrument can also be used for analysis of liquids by using a thin sample cell and by choosing a gas for the detector which has absorption bands in the same ranges as those expected for the desired constituent being measured.

Two papers (*138*, *150*) describe the use of double-beam nondispersive instruments for industrial product control. They include consideration of a number of factors that might be overlooked. Koppius (*150*) provides "a means of visualizing the phenomena occurring in the nondispersive analyzer and derives a general theory for its use in the analysis of mixtures." He uses rectangular plots of intensity versus wave length of each beam. Muly and Heigl (*206*) describe the use of a split-beam infrared analyzer to detect incipient afterburning during the regeneration of cracking catalysts. It measures fluctuations in the carbon monoxide content and can cause the injection of water through rate-action controllers to prevent afterburning.

Other applications include the continuous measurement of alve-

olar carbon dioxide (*39*, *255*), carbon dioxide in assimilation and respiration experiments with plants (*91*), ethylene in the presence of ethane and methane (*215*), and propylene in propane (*216*), and for the automatic control of a catalyst promoter in hydrocarbon conversion processes (*110*).

Peterson (*221*) discussed when to use the nondispersive infrared analyzer for analyses in the laboratory, citing certain advantages even when a spectrophotometer is available. Greater sensitivity may be achieved, since more energy is available if several broad bands are used instead of a single narrow band. The faster response of the nondispersive instrument may also be important.

Visible Absorption Methods. Several papers have appeared on methods of determining gases by measuring the light absorbed. Hawes *et al.* (*123*) have published a description of their flow colorimeter for chlorine analysis. It may be used for either gaseous or liquid samples over wide ranges of absorbancies and can be adapted for operation with any narrow-band filter combination from 350 to 1000 mμ.

Arbogast and Osborn (*12*) have also developed a recording chlorine analyzer for large concentrations of chlorine in process gases. Bertein *et al.* (*37*) described photoelectric analyzers for determining colored gases such as chlorine or nitrogen dioxide, while Wayne and Yost (*278*) used light absorption as a measure of nitrogen dioxide concentration in a kinetic study of the rapid gas-phase reaction between nitrous oxide, nitrogen dioxide, and water vapor.

Photometric measurement of the rate of absorption of dyes has been described by Chamberlain and Lister (*56*), but they found that photometric control of dye concentration in solutions of free dye acids at a pH below 3.5 was not feasible, owing to hydrolysis of the wool by the dye liquor. A British company makes a continuous recording photoelectric instrument for measuring small changes in color of a liquid being used in a chemical process. It is based on the principle of automatic rebalancing using negative feedback.

Guyton *et al.* (*112*) used photoelectric means for continually recording circulatory hemoglobin by passing the blood stream through an optical cell and then back to the animal. The optical system was arranged to ensure correct values for total hemoglobin regardless of its degree of oxygenation.

Ultraviolet and X-Ray Absorption Methods. So little has been published bearing on automatic methods in these fields that both wave-length regions are considered together. A new description has been made of the Beckman quartz spectrophotometer (*27*) modified for continuous recording of percentage transmittance, with an accuracy of ±1%. A special reset circuit provides automatic standardization every 5 minutes.

Suchtelen *et al.* (*261*) have developed a simple apparatus for the determination of mercury vapor in air based on its absorption in the range 210 to 330 mμ. It determines mercury concentrations from 1 to 200% of the danger limit for humans, and it is sensitive also to vapors such as xylene, chlorobenzene, aniline, toluene, benzene, acetone, and trichloroethylene, as well as tobacco smoke and ozone. Glasser's critical review of the ultraviolet method of continuous gas analysis has been published (*103*).

The development of a cadmium sulfide crystal, as a high speed detection device for x-rays, should accelerate developments in this field (*59*). It is claimed that, on an area-for-area basis, the new crystals are over one million times more sensitive to x-rays than are ionization chambers.

Beeghly (*30*) has described an x-ray method for the continuous recording and control of the amount of electrolytic tin coating on steel. It is based on the selection of a wave length which excites significant amounts of secondary radiation in the base metal but not in the coating.

Thermoconductometry. Wider applications of automatic methods based on the measurement of thermal conductivity have been described during the past year. An elementary and historical description (*77*) of the fundamentals has appeared, which classifies three types of mixtures that can be analyzed by thermal conductivity: determination of a single gas (such as carbon dioxide) in air, determination of one gas in some gas other than air (such as hydrogen in nitrogen), and determination of one gas (such as sulfur dioxide) which can be removed from a complex mixture where all gases vary.

Minter and Burdy (*194*) have modified the conventional thermal conductivity bridge so that convection can be combined with conduction to produce a bridge specific to either hydrogen or carbon dioxide in ternary mixtures. Actually, two thermal conductivity bridges are used in their method.

King and Hart (*134*) have described the instrumentation of an ammonia plant in which all gas analyzers operate on the thermal conductivity principle. The Gow-Mac Instrument Co. (*105*) has announced new thermal conductivity cells including a "supersensitive unit" with a signal strength of 60 mv. for 1% hydrogen in air. As low as 16 p.p.m. of hydrogen in oxygen can be measured with an eight-filament, double-output model.

Applications which have been described include sulfur dioxide recording and controlling (*160*), continuous recording of oxygen or hydrogen in boiler feed water (*186*), hydrogen fluoride in the presence of nitrogen and oxygen (*236*), identification of light hydrocarbon gases as they are desorbed from an absorption fractionation column (*50*), and direct determination of oxygen in compounds containing carbon, hydrogen, and oxygen (*118*).

Turbidimetry. Several descriptions of turbidimetric methods for smokes and dusts have appeared. Coolidge and Schulz (*71*) have reviewed the available methods for photoelectric measurement, giving construction details of one- and two-phototube models used at the Pennsylvania State College. They also present a brief theory of light absorption by dust. Shaw and Linsky (*245*) also describe the various methods and instruments used for quantitative measurements of visible smokes and solids discharged from individual sources.

Stoecker (*258*) discussed the correlation between photoelectric cell readings with the weight concentration of smoke as determined by filtration. He found the following factors important: the temperature of the gases at the point where the photocell is installed, the thickness of the column, and the percentage of ash in the solid particles. Each installation must be separately calibrated. Stone *et al.* (*259*) reported a Bureau of Mines study on a photoelectric device for the determination of low concentrations of dust. It was used in connection with a project requiring complete removal of solid and liquid impurities from synthesis gas for the production of synthetic liquid fuels. A commercial turbidimeter (*189*) for measuring the amount of suspended particles in a liquid has been described.

Refractometry. The measurement of refractive index seems to be coming into its own as a useful means of analysis. Thomas' review (*134*, *270*, *271*) describes briefly the methods and instruments that have been used, as well as example applications. He points out two advantages of the reflection-type over the transmission-type refractometers: They can withstand high pressures, and the sample materials need not be transparent.

Svensson (*262*) has continued his studies in refractometry with a description of an arrangement and theory of purely optical differentiation of the refractive index function. Essentially, his instrument is a differential interferometer which gives direct records of the refractive index derivative. The commercially available Precision-Dow Robomatic refractometer is newly described (*191*). A Russian liquid-flow refractometer using monochromatic radiant energy has also been reported (*213*).

New uses of automatic refractometry have been reported for the determination of components in the percolate from an adsorption column (*60*) and for measuring a diffusing liquid in a paper chromatogram (*202*). The latter method uses an instrument which features a five-digit data printer which prints automatically on paper tape at timed intervals.

Polarimetry. Levy (*164*) discussed the automatic measurement of optical rotation and gave the details of a recording polarimeter for studying the kinetics of reactions in which a change in optical rotation occurs. The technique involves measuring the slope of a "rotogram" (recorded graph of optical rotation versus time). Zero-order reactions appeared as straight lines, and the slope was found to be proportional to the concentration of catalysts or enzymes present. Results were given for the determination of penicillin. Levy defines rotography to include all applications based on the continuous recording of optical rotation with respect to some other variable.

Bernhardt's "automatic polariscope" (*36*) is a saccharimeter with a double-field polarizer. Balancing is achieved by converting a modulated beam of light into electrical impulses. The percentage of sugar present in the sample is printed directly on a card to the nearest 0.1%. The instrument has a standard deviation of 0.04 compared with 0.18 for a skilled operator using a manual method, and the reading takes only 9 seconds.

Reflectometry. Three types of applications of the measurement of light reflected from opaque surfaces have been reported. Two patents (*172*, *198*) and one paper (*241*) describe apparatus for measuring hydrogen sulfide in gases, all based on fabric or paper tape impregnated with lead salts which darken in the presence of hydrogen sulfide.

The commercial availability of a humidity indicator consisting of a card with seven colored circles arranged in a vertical column has been announced (*10*). Each spot changes color from red to blue at a different percentage relative humidity, so that the top blue spot indicates the relative humidity to the nearest 10%. Müller and Clegg (*202*) have described the use of light reflection for the automatic photometry of dye mixtures during the development of paper chromatograms.

Conductometry. Many papers have been published during the past year describing automatic conductometric measurement, mainly, of aqueous solutions for determining ionic solutes, and of solids for water content. Gutmann's review (*111*) describes electrolytic conductance bridges. He cites a new method of conductometric analysis depending on the change in Q of an oscillatory circuit which is shunted by a resistance, consisting of a specially designed conductivity cell which, unlike conventional cells, should have a high impedance.

Applications of automatic conductivity measurement described during the past year include: steam purity (*113*, *163*, *187*, *234*), dissolved solids in boiler water (*238*), purity of distilled water (*23*), sulfur dioxide in air (*158*), zinc chloride in the condensation line of an evaporator (*162*), sodium hydroxide in lye peeling solutions (*185*), and dyes in dyeing solutions (*56*).

A patent (*149*) has been issued for a conductometer for measuring the concentration of dishwashing solutions, which is calibrated in such a manner that a glow lamp lights up when the concentration is too low. Balter (*22*), in a discussion of electronics applied to oil exploration, describes an instrument giving "distortion readings" to indicate the presence and concentrations of certain hydrocarbons. Ashman *et al.* (*15*) have described a new recording conductometer for electrolytes, which has good accuracy and high stability for extended periods of time. This was achieved largely by means of thermistor temperature compensation.

The applications for the measurement of water in solids have included: a "drimeter" for moisture testing of fabrics (*95*), moisture in wood or plaster (*264*), and moisture in soil (*148*). One novel moisture tester for grain samples (*51*) has a self-powered ohmmeter which generates its own current, thus eliminating the need for batteries or electric connections. A patent (*140*) covers a continuous method and apparatus for determining water in organic nonionizing liquids. The sample is treated with sodium chloride and the conductivity is then measured with a meter calibrated in percentage of water. It has been applied to the determination of the proof of aqueous alcohol.

Weaver (*279*) has published a complete description of the electrical measurement of water vapor with a hygroscopic film. The method, although not new, did not come into successful use until the development of films of lithium chloride in polyvinyl alcohol on a polystyrene base.

Potentiometry. The use of glass electrodes for potentiometric pH measurement and control has been described anew (*161*, *184*, *246*). Hitchcox (*130*) has written a critical survey of pH meters. Numerous new electrodes are available (*156*) for various purposes and applications including special constructions for high flow rates and corrosive solutions. New instruments include a line-operated plastic-cased (*68*) meter with an automatic titrating attachment, and a pocket-size battery model (*8*) in a Bakelite case approximately 3 × 6 × 2.5 inches, weighing 3 pounds.

Brinker and Williams (*45*) have patented a method for detecting acid anhydride–forming gases, such as carbon monoxide. The air sample is passed through soda lime to remove all constituents except carbon monoxide, oxygen, nitrogen, and hydrogen. The gas stream is then divided into two channels. In one of these the carbon monoxide is oxidized on a heated platinum wire. Both streams of the gas are then bubbled into separate compartments of a cell containing a salt solution. The two compartments are separated by a pervious wall and each has a platinum electrode. The electrodes detect changes in pH which indicate the presence of carbon monoxide in the original air. The apparatus is capable of detecting 1 to 10 parts of carbon monoxide per billion parts of air.

Stein (*256*) has patented an apparatus for measuring chlorine in water at various time intervals. It measures the 30-second and 10-minute component of the chlorine demand. A voltage representing the difference between the two values is used to control the amount of reagent being added.

Measurement of Electric Current. Automatic measurement of electric current is used in a number of methods, including mainly polarography and mass spectrometry. Gutmann's review (*111*) of electronic instrumentation mentions a new method of polarographic analysis which overcomes the inherent difficulties in low-level direct current amplification. A small alternating potential is superimposed on the direct voltage. The alternating current which flows is then amplified in a conventional amplifier.

Breyer (*44*) has described the technique more fully. A plot of the alternating current versus the direct current potential shows a maximum at the normal direct current half-wave potential, and this current is proportional to the concentration of the material being reduced. Three advantages include the facts that dissolved oxygen need not be removed, that reduction potentials only 40 mv. apart are separable, and that the alternating current differential current is larger than the direct current–diffusion current, which leads to improved reproducibility. These improvements would seem to accelerate the use of current measurement in automatic analyses.

Offutt and Sorg (*214*) described a direct-reading polarograph for the determination of tetraethyllead in gasoline. Two papers have appeared describing methods for the continuous determination of oxygen in chloride-containing fluids (*83*) and in small quantities of gas (*151*). The latter determination is based on an oxygen-depolarized carbon electrode in potassium hydroxide. Hazey (*127*) has described a continuous amperometric measurement of residual chlorine, directly in parts per million. Drake (*86*) has employed polarographic methods for automatic recording in the chromatography of proteins.

Richardson (*228*) has patented an apparatus for the continuous determination of oxygen in flue gas. It consists of a burner to which predetermined proportions of the sample gas and a fuel gas are conducted. An annular electrical contact surrounds the flame and the current flowing in a circuit including the burner and the contact is measured. A continuous gas analyzer of the glow-discharge type (*24*) has been patented by Becker. Gas is

fed at a reduced pressure to a globular shell in which a pair of heated electrodes is located. When a sample changes the electron flow across the electrodes, a current-measuring device responds. A leak detector (*84*), based on the fact that hot platinum emits positive ions in the presence of infinitesimal amounts of halogen compounds. has been announced.

Increasing evidence of the application of mass spectrometric methods to the continuous monitoring of gas streams has appeared during the past year. Munch (*207*) has described developments during the past several years, but states that the instruments required are so expensive that they will be used only when there is no other means available. He expresses the hope that other types such as the Bennett radio-frequency and "omegatron" or ion-resonance types will prove simpler, more compact, and less expensive. Neither type has had adequate testing of its value for the continuous monitoring of process streams.

Robinson *et al.* (*235*) describe a magnetic-deflection mass spectrometer designed specifically for industrial process control. It records only a limited number of preselected mass peaks and periodically standardizes itself against a known sample. Miller *et al.* (*180*) have used a mobile mass spectrometer to provide a continuous record of the nitrogen content of expired gases. Another application of the mass spectrometer has been reported (*62*) for the continuous monitoring of single components and for the analysis of multicomponent gas mixtures.

Measurement of Dielectric Constant. Both Gutmann (*111*) and Thomas (*134, 271, 272*) in their general reviews have stressed the usefulness of measurement of the dielectric constant in automatic analysis. It has been especially applied to the measurement of moisture in various materials, although Gutmann also mentioned an apparatus for butterfat in milk. Thomas states that the dielectric properties of organic materials are important and easily measured, but have received only limited attention.

Electrical capacitors of the rod-and-cylinder type are especially useful for the "dielectimetric" measurement of continuous-flowing liquid samples at several atmospheres of pressure. The liquid is passed through the capacitor element, forming part of an oscillating circuit. Changes in the composition of the sample then cause changes in the oscillating frequency, and it is convenient to measure this frequency change with a frequency meter. Another arrangement has an oscillating circuit with two capacitors, one for the sample and the other forming part of a recording bridge system. Changes in the dielectric constant of the sample cause changes in the vibration frequency of the circuit, and automatic adjustment of a compensating capacitor actuates the recorder. Thomas further mentions applications for water, alcohol, or phenol in hydrocarbons, and paraffins in naphthenes, aromatics, or other hydrocarbons.

Engelder (*92*) has described the continuous recording of the water content of oil-field emulsions, and Asbach (*14*) developed a similar method for coking coal.

Babb (*18*) described a moisture meter, using radio-frequencies of about 10 megacycles per second, designed primarily for samples of a vegetable nature. He emphasized that there is no simple relationship between permeability and moisture content, and hence the instrument must be calibrated with each type of sample. A new portable instrument has been announced (*116*) which has a temperature-compensated battery-powered circuit designed to measure the moisture content of cereal crops. A portable wood-waste moisture meter (*195*) features a nondestructive gun-type electrode having a penetration of 3 inches. It tends to average out the moisture content directly beneath the electrodes.

Measurement of Radioactivity. Nier *et al.* (*211*) have described a recording ionization chamber for determining traces of radioactive gases. It has been applied to the continuous determination of uranium hexafluoride in nitrogen for concentrations between 10^{-5} and 1% uranium hexafluoride. Williams and Smith (*286*) used a continuous-recording scanning device for radiochromatographic analysis of labeled compounds. The actual measurement was of the radioiodine in compounds adsorbed on paper strips. Müller and Wise (*203*) used beta-rays for rapid analysis of labeled paper chromatograms. The detector was an ionization chamber connected through a pulse-integrating counter to a recording potentiometer.

DATA

Numerous advances in the problems of collecting, storing, and using large amounts of quantitative data have been reported during the past year. Analysts concerned with automatic analysis will be interested in the wide variety of new curve-recording devices which are commercially available. These include the plotting of the continuous relationship of two independent variables (*188, 204, 220*), a direct-writing recorder amplifier for inkless recording of the electric unbalance of a resistance bridge (*21*), an oscillograph which will record three variables on 70-mm. film or paper (*133*), a photopen recorder to record directly the motions of a galvanometer or other mirror-type instrument (*28*), inkless (heat-writing) current or voltage recorders (*181*), two-pen recorders (*157*), a multipoint recorder which uses a nonbalancing method of detecting changes in a measurable circuit (*280*), a null-balance strip-chart recorder for any variable that can be measured in terms of impedance (*47*), a cathode-ray tube which can measure any phenomenon that can be translated into electrical impulses and is capable of measuring pH differences of 0.001 (*7*), a stabilized direct current indicating amplifier (*159*), a key-wound portable recorder designed for use with a tachograph (*287*), and a magnetic tape recorder for storing information in a small space (*40*).

Loucks (*170*) has reviewed high-speed direct-trace recording methods, with suggestions on how to avoid troubles arising from the inertia of the moving stylus in conventional ink writers or from the tendency of servo-motor systems "to hunt." He tabulates the merits of four types of fixed-stylus recorders and two types of moving-stylus sweep-balance recorders.

Various attachments or modifications have been described, including: ball-point pen accessories (*192*) which prevent smudging when lines are close together or provide duplicate graphs with the use of regular carbon paper (*121*), range selectors for strip-chart recorders for mass spectrometers (*49*) or Raman spectrometers (*240*), and new facsimile recording papers (*5*).

The wider use of data printers has been urged by Müller and Zenchelsky (*204, 205*), and a new electric indicator and printer (*100*), intended mainly for use with low resistance strain-gage devices, prints full block figures on cards or tape. It has been used for electric weighing and can record remotely.

A new device (*4*) for compressing the length of long curves reduces the time necessary for their appraisal. A digital reader (*167*) reads test instruments at high speeds and records the reading on tape or punched cards. It samples a varying input voltage at rates up to 50,000 times per second and converts these readings into seven-digit binary form. It has been used to convert experimental data into binary digit form for feeding into computers and reconverting the computer output into analog form for recording as a graph.

A "teleplotter" (*266*) has been described which plots curves from digital data furnished in the form of IBM cards or introduced by means of a keyboard. A photoelectric "reading head" counts the lines and spaces on the graph paper in each of two perpendicular directions. It plots 40 points per minute on linear or logarithmic paper, and five different symbols can be used to plot five curves on the same graph.

Computer design and operation are rapidly becoming important. The latest developments of high-speed computers and their applications have been reviewed (*57*). Morris and Bubb (*196*) have made suggestions as to how analogical computing devices can serve the process industries. Müller (*200*) has pointed out how analog computers can save time and expense by process

simulation. A new ball-and-disk integrator (*165*) has been announced as a computing element for analog computers which can generate derivatives, integrals, reciprocals, products, squares, exponentials, and trigonometric functions.

McEwan and Skolnik (*175*) developed an analog computer for flame gas composition, based on the fact that the reaction equilibrium constant is equivalent to two ratios which may be represented on a Wheatstone bridge circuit by making three arms proportional to the partial pressures of the molecular species involved and the fourth arm proportional to the equilibrium constant. The computer simulates electrically the conditions of temperature, pressure, and composition of the combustion products, which are impressed as resistance in a series of interlocking Wheatstone bridges. When the bridges are balanced, the resistances proportional to the partial pressures are produced. The instrument can also convert these partial pressures into mole fractions. Representative results are given for ten gaseous constituents at a reaction temperature of 3000° K.

Reports on progress in the problem of classifying infrared spectra on cards have been given by Creitz (*74*) and by Shreve and Heether (*248*).

Walker in an article "Blueprint for Knowledge" (*276*) predicts the future development of the automatic library, where televised or microfilmed information may be sent out to home or office subscribers from central libraries. He states that four technical problems will have to be solved before such a development will be possible: the "electrecord," an electronic means of storing visual or oral information; an "Autolibrarian," a dialing mechanism for selecting the desired information; a "pocket index to world knowledge" for selecting the proper code number to dial in; and "books without cost," printed information so cheap that it would cost less to throw it away than to store it.

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Development of an Efficient Analytical Record System

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One of the most important factors in the successful operation of an industrial analytical laboratory is an adequate system of keeping records of samples being analyzed and of the data obtained. The system described has been developed to meet this need and is in actual use in several industrial laboratories. Printed slips with interleaved carbons are used for recording and reporting analytical data. Printed punch cards are also used, first to provide positive control of the progress of the analysis and then to locate original data on the report slips in the permanent file. The system is sufficiently flexible to be useful in large or small laboratories handling a wide variety of analytical work. It is convenient and time-saving for analysts and supervisors, eliminates much handwriting, and gives information leading to improvement of analytical organization helpful in compilation of operational reports.

THE analysis of the wide variety of samples which originate in an industrial research laboratory presents many problems to supervision. Provision must be made for adequate space and equipment, for manpower adequate in training as well as in numbers, for analytical research and the development and writing of analytical methods, for an easily operated time-accounting system, and for intelligent assignment and supervision of the work if analytical results are to be determined accurately and reported promptly. All of these factors are important in promoting smooth operation of an analytical group, but in the authors' experience one of the most important factors is the provision of an efficient record-keeping system for the samples submitted and analyzed. Under such a system the samples will be assigned without delay to the proper analysts who will then record data and results with a minimum of writing in a form meeting patent requirements. The system must also provide for reporting the results promptly and for filing the data so that they will always be quickly accessible.

There are many differences in detail in the operation of industrial laboratories which make it necessary for each one to provide a record-keeping system especially designed to meet its own needs but the general principles involved are universally applicable. A record system will be discussed which has been developed over a number of years and used in several of Du Pont's analytical laboratories. General principles will be emphasized but enough details will be given to illustrate the way the system works under a given set of conditions. Although the authors are responsible for the basic design of the system, numerous suggestions have come from those using it which have improved its workability and efficiency.

Several objectives should be kept in mind in the design of a record-keeping system.

1. Reduction of analysts' clerical work.
2. Clear-cut assignment of determinations.
3. Concurrent attention to different determinations on a single sample.
4. Positive check on status of work in progress at all times.
5. Prompt reports to sender of sample.
6. Clear, concise, original data, filed in a readily accessible manner.

In this discussion the term "chemist" is used to designate one who submits a sample for analysis and the term "analyst" is used to designate a chemist who analyzes a sample.

ANALYTICAL RECORD FORMS

Each sample submitted for analysis bears a special label designed and furnished by the analytical group (Figure 1). The label has spaces for all of the information required in processing the sample. A space may also be provided for description of hazards or for special handling instructions. This label usually constitutes the only request made by the chemist for performance of the analysis, although chemists are encouraged to discuss any unusual aspects of the sample in advance with an analytical supervisor. All samples are delivered to the Analytical Records Office where a serial number is assigned and marked on the label. Analysts in the laboratories may not accept samples directly for analysis except under most unusual circumstances.

PC NO. 5678 Date 4-24-51
Sample of Benzylisothiourea hydrochloride
Designation 3075-24 Proj. 1057
From Johnson Bldg. Lab. No. 177/23

Analyze For	Est. Amount
C & H	47 + 5%
Cl	17%
N	14%

Figure 1. Analytical Label

The two forms on which records of the analysis are kept have been designed so that all of the information required in handling the sample can be typed in a single operation. This reduces to a minimum the amount of writing which must be done by the analyst in the laboratory.

One of these forms, which would be used for the sample shown on the label in Figure 1, consists of two white and two yellow printed analytical report slips with interleaved carbons attached firmly to a perforated tab at the top of the sheaf of slips. Space is available on the upper half of each sheet for the information which appears on the sample label. The top sheet which is shown in Figure 2 is used for making a final typed report of the analysis to the chemist. The second white sheet and the two yellow sheets are available for the three analysts who will make the three determinations requested on the illustrated label. If only one analyst is to work on a sample, a sheaf of slips would be selected by the typist having only two white printed slips and one interleaved carbon. An alert typist learns quickly by experience to provide a sheaf with the proper number of slips for each sample. Sheafs of slips are provided having none up to four yellow slips in addition to the two white slips, thus providing for the assignment of samples to any number of analysts up to five. Dimensions of the slips are $3^3/_4 \times 6^3/_4$ inches not including the perforated tab at the top.

The second form used is a 5×8 inch punch card which has several functions (Figure 3). During the analysis it supplies readily available information about the sample, the assignment of determinations, and the progress of the analytical work. Following completion of the analysis, the card is punched to provide a ready means of finding the analytical report in the files. Furthermore, the punched card can be very useful in compiling a variety of data concerning the operation and efficiency of the laboratory.

The headings on the left side of the card correspond exactly with those on the report slip (Figure 2) so that when a piece of carbon paper is placed on the card and the sheaf of slips is placed over it, typing of the information on the sample label can be performed in one operation. Determinations to be made are typed on the right side of the card and on the lower half of the slips. The serial number of the sample and name of the chemist are typed on the lower right edge of the card. The carbon papers are removed from the sheaf of slips and the original or top slip is retained by the typist and will be used by her for preparation of the final typed report of the analysis to the chemist. The remaining slips and the card together with the cards and slips for other samples are placed on the supervisor's desk. The samples are placed on a central shelf in the order of assigned serial numbers.

ASSIGNMENT AND ANALYSIS OF SAMPLES

The supervisor assigns the determinations to be made on each sample to one or more analysts by stamping the initials of the ana-

P. C. No. DATE RECEIVED

POLYCHEMICALS DEPARTMENT
ANALYTICAL REPORT

SAMPLE OF

DESIGNATION

CHARGE P-

SENT BY

DATE REPORTED

ANALYSIS

ANALYZED BY

V-2195

Figure 2. Analytical Report Slip

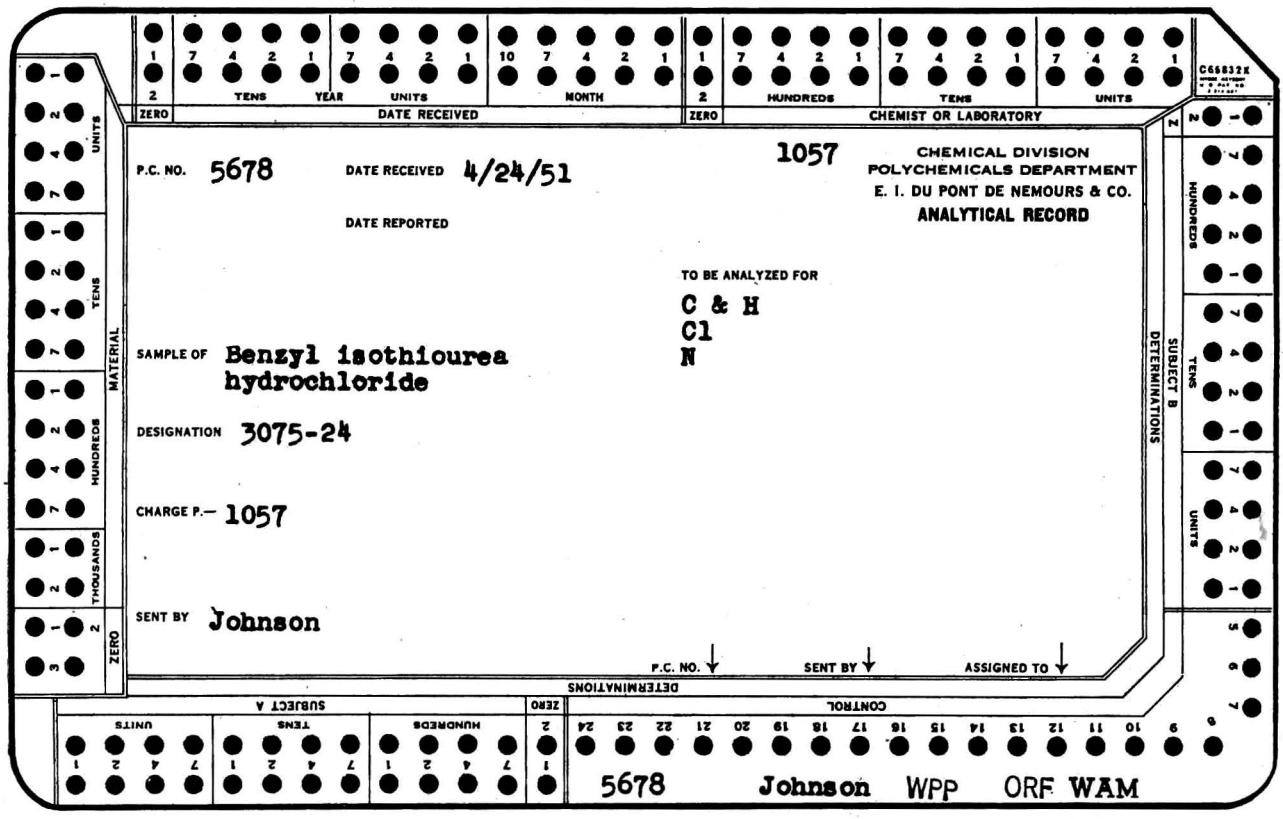

Figure 3. Analytical Punch Card

lysts on the lower right edge of the punch card as shown in Figure 3, and in front of the determinations on the three carbon copy slips. Thus he prepares a copy of the slip for each analyst who will work on the sample. The supervisor then hands the slips to the assigned analysts who place them in individual loose-leaf notebooks. Contrary to custom, the holes in the slips are on the right side of the front of the sheet rather than on the left. Most of the handwriting involves recording data on the back of the slip. It is easier for a right-handed person to enter the data when the right hand does not have to rest on the rings of the loose-leaf notebook as would be the case when the holes are on the left of the front of the sheet.

The individual analyst thus has in his loose-leaf notebook at all times a complete record of all of the work currently assigned to him. Each slip has on it all of the available information concerning the sample and the kinds of determinations to be made in addition to those assigned to him. This allows him to group similar samples and plan his work in the most efficient manner. In most cases he can go to the central sample shelf in the morning and easily select the samples he requires during the day. If other analysts are to make determinations on a sample he returns it to the sample shelf as promptly as is convenient.

The analyst records all data pertaining to the analysis in ink on the back of the assigned slip (Figure 4). This includes all weighings, buret readings, and other data required in the final calculations as well as pertinent observations and each entry is dated. If there is insufficient room on the back of the sheet a second blank sheet of yellow paper is used on both sides after entering the serial number at the top of the sheet. Modifications of standard procedures or special procedures used are outlined briefly.

When the determination is complete the results only are entered on the front of the slip and the analyst enters his initials at the bottom as shown at the left of Figure 4. In some analyses data are recorded on strip charts or on large specially designed forms which are then filed in regularly maintained files. In such cases the results are entered on the front of the analytical slip and only the file number referring to the data is placed on the back.

The results obtained are usually telephoned by the analyst to the chemist as soon as the determination is complete. The disadvantage of an occasional misunderstanding of quoted figures is believed to be offset by a prompt report of data as soon as it is available and by the opportunity for a discussion of the analysis between the chemist and the analyst. It is understood that the telephone report is informal and does not necessarily take into account other determinations being made. After reporting the result by phone the analyst takes the sample bottle, if he still has it, and the completed slip to the pocket drawer file (Figure 5).

STATUS OF ANALYTICAL WORK

The pocket drawer file is a very satisfactory means of following the progress of the analysis of many samples. The punch cards are placed by the typist in the file serially as soon as the work is assigned. The lower edge of each card is always in view and shows the serial number, the name of the chemist, and the initials of the analysts assigned to work on the sample. Full information concerning the sample can be obtained simply by raising the pocket which exposes the face of the card. The analyst examines the card in the file corresponding to his completed slip. If his determination had been the only one requested by the chemist, as he would see by observation of the initials stamped on the card, he would place his slip in the pocket in front of the card, thus indicating completion of the analysis. He would then place the sample bottle on a central shelf for analyzed samples where it would be held for 1 week and then returned to the chemist. This keeps the sample available for further analyses or rechecks.

If the card shows that other analysts are still working on the sample, since there are initials not yet crossed off, he crosses out his own initials and places his completed report slip behind the card. The sample bottle is placed back on the central shelf for unanalyzed samples.

If the card shows that other analysts assigned to the sample have completed their work and crossed off their initials, the analyst reaches behind the card, removes the completed slips, and files them with his in front of the card thus indicating completion of the analyses. He then places the sample bottle on the central shelf for analyzed samples.

Once or twice each day the typist goes through the file and removes the cards and slips wherever a slip is on top of the card indicating completion of that sample.

There are eight pocket drawers in one unit and four units are convenient for a volume of about 400 samples per week (Figure 6). Each drawer holds 50 cards. The cards are filed serially beginning with the top drawer on the left and continuing down the left side. Then the top drawer on the right is filled and filing continues down the right side. By the time cards are filed in the bottom drawer on the right analyses will have been completed for most of the cards which were on the left side. The top drawer on the left is then labeled as an "old samples" drawer and the cards for the few "straggler" samples left are moved to the old samples drawer. The empty drawers on the left are then removed and the drawers on the right are then moved in order to the left. The empty drawers are installed on the right and are ready for more cards. The file is thus a working rotating file.

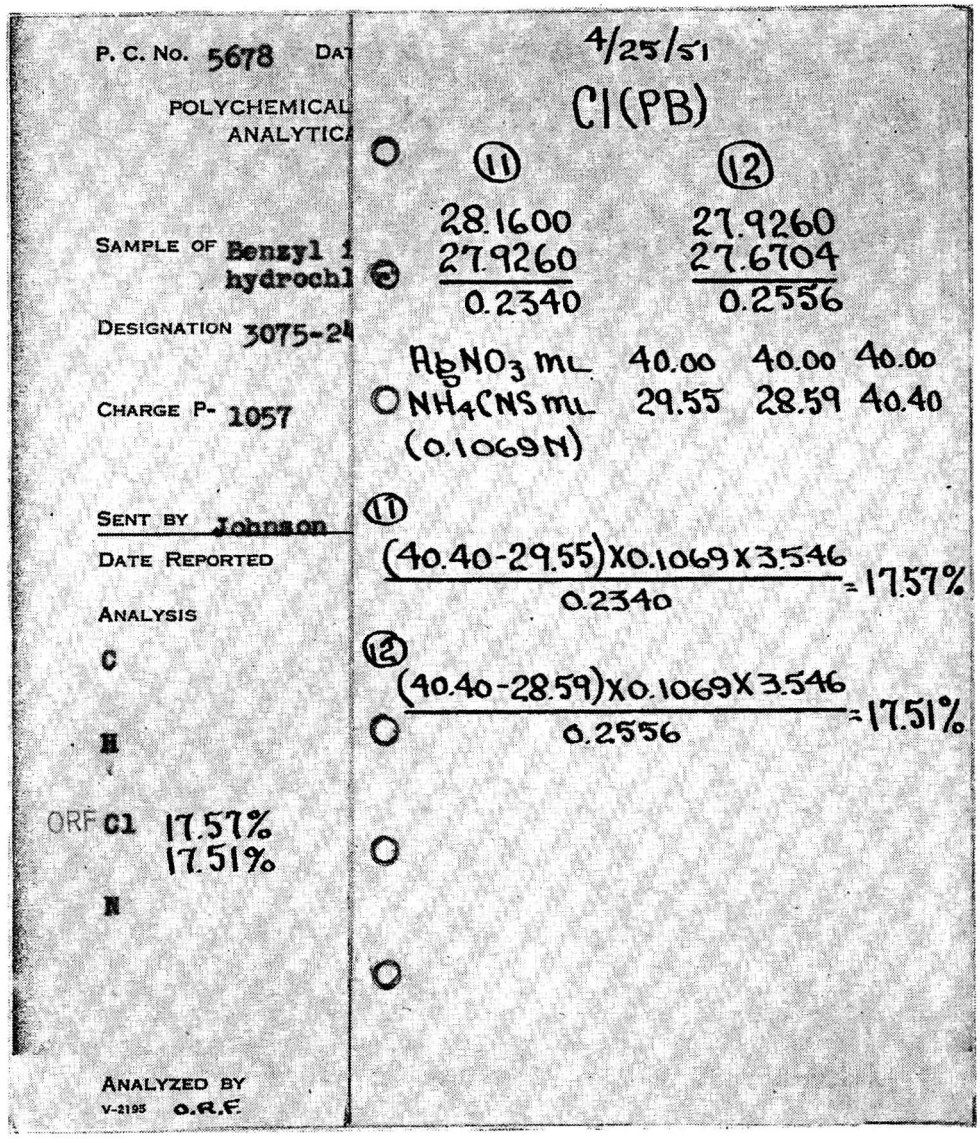

Figure 4. Record of Original Analytical Data

Much information concerning operation of the laboratory is continually available from this file. It is easy to obtain figures for the total number of samples received in a certain recent period, the total reported, the total on hand at a certain time, or the total on hand which are 1 week old or 2 weeks old. The nature of the various samples on hand is easily ascertained and information concerning a particular sample is always up to date since one can tell who is assigned to work on it and, if several analysts are working on it, which ones have completed their work. If the sample bottle is not on the central shelf the file will show which analysts may have the sample. Supervisors can tell at a glance which analysts are overloaded or falling behind in their work and thus shift new assignments to equalize the load.

All individuals concerned with the operation of the system—clerks, analysts, and supervisors—should be watchful for time-saving short cuts which can be applied very frequently without reducing the effectiveness of the system. For example, if five samples, all of the same material, are received from one chemist at one time for similar analyses, it may be possible to prepare only one slip and one card, allowing five serial numbers for the lot as in 5670–4 (Figure 5). If there is not room to report five results on one slip, two or more slips may be prepared but still only one card will be required.

After removing the completed slips and corresponding card from the card file, the typist stamps the date on the white copy and the punch card and checks to see that the card lists all of the determinations which were made. The analytical slips representing the various determinations on a single sample are clipped together with staples. The original white report slip, corresponding to the analytical slips, is then removed from the file of unreported slips and the results on the analytical slips are typed on the report slip (Figure 7). The slips are then sent to a supervisor who inspects the results and, if he wishes, the data and then after approval places the report slips in the mail for the chemist and returns the analytical slips to the typist who files them by serial number in a permanent file.

PERMANENT FILE OF ANALYTICAL DATA

The information on the completed analytical slips is all original data which is written in ink; the slips are dated, signed, witnessed, and bear serial numbers. Such information is frequently valuable corroborative evidence in patent work and, therefore, it is necessary to be able to find any slip in the completed file with a minimum of searching. Furthermore, the analysts themselves

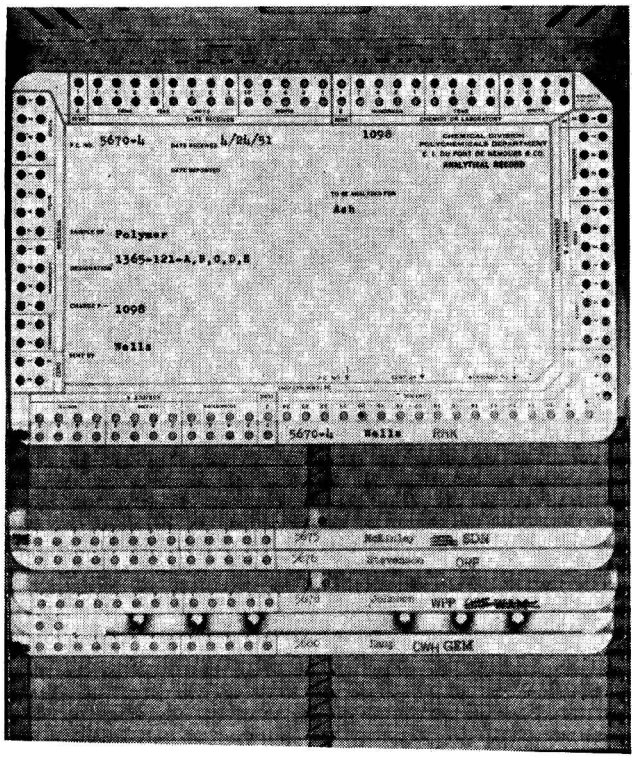

Figure 5. Punch Cards in Pocket Drawer File

often wish to refer to previous work in devising analytical procedures for new samples.

In past years these slips were filed in accordance with the name of the material but this was very cumbersome as were several other methods. The authors' solution for this difficulty works very satisfactorily and consists of filing the slips by serial number and then using the punch card to determine the serial number of the particular analytical slip desired.

Although this punch card system is rather widely used a short explanation of the principles on which it is based is in order for the benefit of those unfamiliar with it. The information on the cards is reduced to numbers by means of code lists (Figure 8). In the system described here there is one code list for the chemist or laboratory submitting the sample, another for the material of which the sample is composed, and a third for the determinations

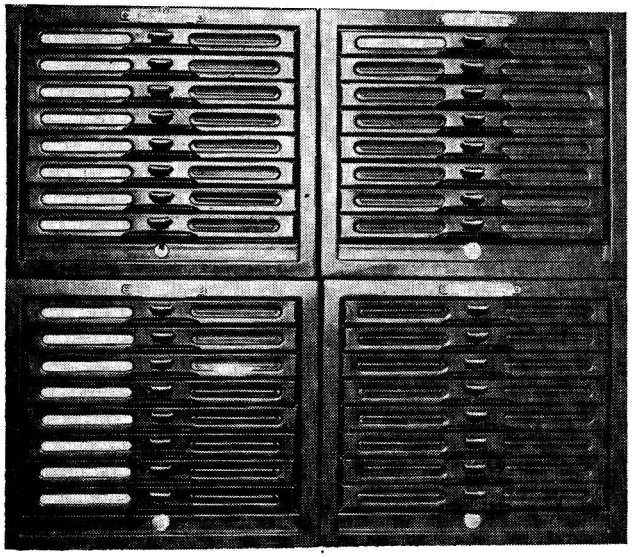

Figure 6. Pocket Drawer File

made on the sample. Since the date on which the sample is received is already a number, it can be punched out in the other block directly. The card is coded and punched after the analysis is complete.

Using the code block in the upper right corner for chemist or laboratory as an example, the number assigned to "Johnson" in the code is 403. The 4 in the hundreds block is punched out to the deep hole since, on the card, the 4 is not obtained by a combination of two smaller numbers in the hundreds block. No

P. C. No. 5678 DATE RECEIVED 4/24/51

POLYCHEMICALS DEPARTMENT
ANALYTICAL REPORT

SAMPLE OF Benzyl isothiourea hydrochloride

DESIGNATION 3075-24

CHARGE P- 1057

SENT BY Johnson

DATE REPORTED APR 2 7 1951

ANALYSIS

C	47.38% 47.46
H	5.44% 5.48
Cl	17.57% 17.51
N	13.92% 13.81

AHH

ANALYZED BY WPP ORF WAM

V-2195

Figure 7. Completed Analytical Report Slip

number is punched out in the tens block since this digit is 0. The 2 and 1 are punched out to the shallow holes in the units block since two small numbers must be used to make 3. The zero block shows the total zeros in the number and one zero is punched.

In sorting a stack of cards for those cards coded 403, a long needle is run through the 4 deep hole for the entire stack. When the needle is raised all of the cards punched 4 deep fall out. The cards which have fallen out are arranged in a stack and the needle run through the 2 shallow hole in the units block. The cards that fall out are again stacked and the needle run through the 1 shallow hole. A final sort is made through the 1 zero hole. These operations can be done rapidly and will sort out of the pile only those cards coded 403.

Only the year and month are punched for the date in the upper left corner since, in looking for data for a particular sample, it is unlikely that the exact date of submission will be known.

The material block at the left has space for 4000 numbers which are enough to include all the kinds of samples that might be received. Some of the samples are relatively pure organic com-

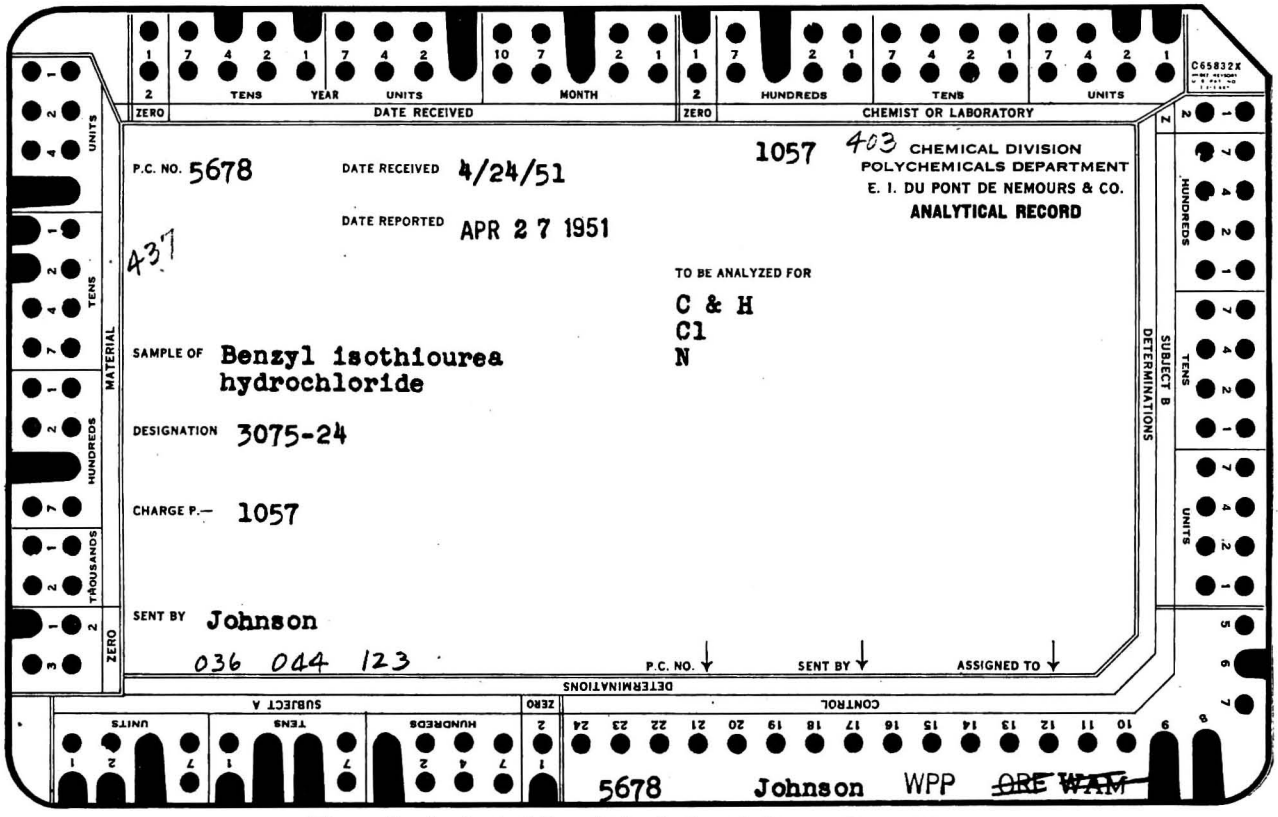

Figure 8. Analytical Punch Card after Coding and Punching

pounds named according to principles usually followed in *Chemical Abstracts*. The authors have coded the organic compounds to correspond with the paragraph numbers in the 1945 "Introduction to the Subject Index of Chemical Abstracts," entitled "The Naming and Indexing of Chemical Compounds" (*1*). This requires a block of about 500 numbers which provides only for the numbering of classes of compounds. No attempt is made to number individual compounds.

A block of 700 numbers is set aside for assignment to inorganic compounds. A number is assigned to each element, leaving several unassigned numbers after common elements for probable assignment to compounds of the element.

Other blocks of numbers are set aside for assignment to materials in various fields for which there is particular interest—for example, in the plastics field a general number is assigned to nylon. Closely following numbers are assigned to diamines, dibasic acids, nylon salts, salt solution, polymer, molding powder, molded parts, and extruded parts. Other polymers are treated in a similar fashion. Then comes a section on polymer modifiers such as colors, dispersing agents, fillers, inhibitors, plasticizers, stabilizers, and the like. In general, numbers are not assigned to particular substances but to classes. Common classes usually have unassigned numbers immediately following for assignment to particular members of the class at a later date if it seems desirable. Every effort is made to keep the code as brief and simple as possible.

In the three codes described thus far only a single number is selected for each sample. However, it frequently happens that several determinations are made on each sample and the "Determinations" block, covering two sides of the card, is set up so that up to eight or even ten numbers can be punched. This is done by punching up to four or five 3-digit numbers in the *A* block at the bottom left regardless of interferences and then punching the sum of the three digits in each number in the adjacent control block at the bottom right. Thus on this card the numbers 036 for C and H, 044 for Cl, and 123 for N are punched in the *A* block regardless of interferences and then the sums of the digits—9, 8, and 6—are punched in the control block. By sorting for the sum of the digits as well as the number no difficulties and few interferences are encountered. Four or five numbers may be entered in *A* and a like number in *B* at the right side using the same control block for both. All numbers whose digits total between 1 and 4 or 25 and 27, inclusive, have been dropped out of the code list to save space on the card. Elimination of these seven sums of digits removes only 44 numbers from the 999 available for determinations.

In the determinations code the first 200 numbers are assigned to the elements and thus about 100 numbers are available for assignment to common inorganic compounds of the elements as required. Three hundred numbers are assigned to determinations of organic compound classes and functional groups followed by a hundred numbers assigned to physicochemical determinations. This leaves about 400 numbers, largely unassigned, which are available for miscellaneous and special analyses.

As with the materials code, every effort is made to keep the determinations code as simple as possible. A number is not assigned to a new determination if it is possible to fit it into an existing classification. As a result typists with no formal education in chemistry can be trained to code 90% of the cards for the materials and determinations classifications and all of the cards for the date and chemist classifications. Technical assistance is provided for assigning code numbers when necessary. Since the typists quickly become familiar with the code numbers commonly used in each classification, the coding and punching of the cards is a relatively rapid operation.

After the cards are punched, they may be filed permanently in accordance with one other category, such as the research project under which the sample originated. Thus if one or more of the five different classes of information is available about a particular sample, the card can be found quickly and from it the serial number of the analytical slip which contains the desired information. This slip can then be found quickly in the permanent file.

Finally the cards filed over a period of time can be used in the compilation of much data concerning the operation of the laboratory which is of value in planning the scale of future operations or in preparation of reports. It is a simple matter, for example, to find the number of samples analyzed for any one chemist or group of chemists or to ascertain the number of samples analyzed for a particular determination.

SUMMARY

An analytical record system is presented which involves the use of a specially designed label for samples submitted for analy-

sis. Information on the label is transcribed in one typing operation to printed analytical report slips, with interleaved carbon paper, and to printed punch cards. The report slips are used for recording, reporting, and filing the analytical data obtained. The punch card is used first to indicate the progress of the analysis and subsequently to find the original data in a permanent file by a simple hand-sorting procedure. Four categories of information are punched by hand into the card from code lists. This flexible system is applicable to a large or small volume of a wide variety of samples and provides positive control of the progress of the work. It gives much information which leads to improvement of the analytical organization and is helpful in the compilation of operational reports.

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Industrial Analytical Research

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Hercules Powder Co., Wilmington, Del.

The basic elements necessary for analytical research to fulfill its role in industry is discussed herein. The operation of an industrial analytical research group at the Experiment Station of Hercules Powder Co. is cited as an example. The authors also discuss the types of problems handled, specific talents needed in a well-balanced group, and outlets into other fields. Finally, a few suggestions are offered on the training of personnel for this type of work.

THE basic elements necessary for analytical research to fulfill its role in industry can best be discussed by first describing the operation of an industrial analytical research group. The integration of its activities with other units of the research organization can thus be shown.

ANALYTICAL LABORATORY

The analytical research group at the Experiment Station of Hercules Powder Co. is a unit of a general analytical division similar to those existing in a number of large industrial organizations. In all, there are about 75 people in the division. Of the total, 55 are college-trained chemists or chemical engineers; 11 have doctorate degrees, and a number of others have master's degrees or other graduate training. The principal functions of the Analytical Division are:

1. To determine the composition and physical properties of samples of research materials and generally to handle analytical problems arising in manufacturing and sales.
2. To develop new methods and techniques that are required for the aforementioned and provide consulting service to all departments of the company relating to chemical analyses.
3. To develop, standardize, and keep up to date the methods used in the company's plant control laboratories.

The manner in which the Analytical Division is organized to carry out these functions is illustrated in Figure 1.

The Standardized Analyses Section, which includes about two thirds of the total personnel, may be looked upon as the division's production unit. This section, however, is in no sense to be compared to a routine control laboratory. It receives 2000 to 3000 samples per month, nearly all of them of a research character, whose handling requires judgment and ingenuity of a high caliber.

The Laboratory Standardization unit standardizes and checks upon the work of the plant control laboratories, edits specifications for materials, and through cooperation with trade associations and societies keeps the company's analytical methods "in tune" with those of the industry.

The other two sections—Methods Development and Physical Chemical Measurements—are organized primarily for research. The former is concerned mainly with the composition and the latter mostly with the properties of matter, although there is no hard and fast dividing line. The personnel with doctorate degrees is concentrated in these sections. In this discussion the work of these units will be given the major consideration.

FUNCTIONS OF ANALYTICAL RESEARCH GROUP

The development of new methods and techniques, and the handling of special analytical problems is the particular concern of the Analytical Research Sections. New products and processes mean new analytical methods. Practically all research is dependent upon analytical data for guidance, and it becomes increasingly evident that the progress of most research projects from conception through pilot plant operation is contingent upon the aggressive application of new or improved analytical techniques. The analytical research group must keep abreast of the latest techniques and bring them into use wherever they will aid in the solution of a research problem or make possible simpler plant control.

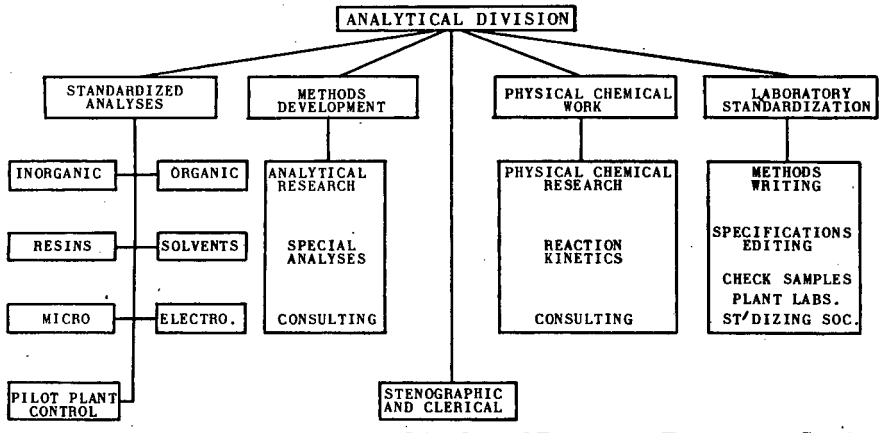

Figure 1. Organization of Industrial Analytical Division at Experiment Station of Hercules Powder Co.

TYPES OF PROBLEMS

The problems encountered by this group may originate in any of the broad fields of the company's interest, such as cellulose and cellulose products, explosives, synthetic resins, insecticides, ter-

penes, or rosin and its derivatives. Examples selected from the work of the group over the past few years include the development of new methods for analyzing mixed styrenes (*4*); for the determination of conjugated dienes in pyrolysis products from the cracking of terpenes (*9*); determination of total volatiles in smokeless powder (*10*); determination of carboxymethylcellulose in paper (*5*); and for the direct determination of oxygen in organic compounds (*1*). Examples of published papers from this group also include: "Potentiometric Titration of Weak Acids in Ethylenediamine" (*8*), "An Adiabatic Calorimeter" (*11*), and "Present Status of Intrinsic Viscosities" (*3*). These examples illustrate the wide variety of the work with respect to its technical content.

The problems may be long range or short range and vary from the development of a new method needed in an exploratory research program to the identification of a residue . . . from reaction kinetics measurements to determinations of explosive limits of various gaseous mixtures. Again, the problem may be to select and develop suitable analytical methods needed for the evaluation of a proposed process in the pilot plant, where the requirements may be considerably different from those existing during the laboratory development, and similarly to develop from this stage the most suitable control methods for subsequent plant production.

PERSONNEL REQUIREMENTS OF OUTLETS INTO OTHER FIELDS

These illustrations which show the wide scope of the work make it easy to see the need for a good balance of talents in such a group. While the men are mainly analytical and physical chemistry majors, there have nearly always been one or two organic chemistry majors included in the group. In other words, in addition to requiring the "know-how" on ways and means of measuring and determining, help is needed in selecting reactions that might be made the basis of quantitative methods. Here, especially, the organic training is helpful.

The need for flexibility in the personnel is emphasized. The job may be a 2-day or a 6-month one; it may require the individual attention of the analytical research man or it may be one of several jobs which he will carry concurrently. In some cases men will be temporarily assigned from the Standardized Analyses Section to assist him on the problem. This practice fosters close cooperation between these two sections of the division and is mutually beneficial in developing the talents of promising men in each group. This flexibility must also be combined with good judgment and "horse sense." One must discriminate between those cases where the highest precision and accuracy that can be achieved are necessary and those where an approximate result will provide an entirely suitable answer. Individuals who look upon variety and change as a challenge and not as an annoyance are preferred. If, broadly speaking, all "researchers" were divided into two general types, then those favoring the philosophy of learning a "little about a lot," rather than a "lot about a little" would be the type most suited for this work.

What about the development of the individuals engaged in this type of work? It is apparent that these men in the course of their work must make a rather wide circle of contacts within the company. They necessarily gain a considerable familiarity with many of the research programs, process developments, and technical service activities of all the company's operating departments. This group is perhaps one of the best places in the research organization for acquiring, in a relatively short time, a reasonably good over-all picture of the company's technical activities. This situation leads naturally to a number of possible outlets for the personnel—for example, a former member of the group has recently progressed into the position of chief chemist at one of the company's largest plants; others have been transferred to development groups at the plants, or in some instances, directly into production. Some have moved into supervisory positions in the research divisions of the various operating departments. A few have gone into sales and into liaison groups such as sales-research.

CORNERSTONES OF ANALYTICAL RESEARCH

The basic elements necessary for the successful operation of such a group are as follows: First, there must exist in management an attitude which puts analytical research on the same basis as any other type. To put it another way, the emphasis is on research and not on whether it is physical, organic, or analytical. Secondly, and this is really a consequence of the first point, analytical research chemists must have an equal status with research chemists in any other line. They should be considered as full members of the research team. With respect to selection of personnel for this work—classification, salaries, and opportunities—all are considered on the same basis as for research chemists assigned to any other research division.

Other helpful features follow once these attitudes prevail. There is a clear-cut separation between the analytical research and the standardized analytical work. This does not mean that the research unit operates in a cloistered atmosphere, oblivious to the work of the standardized analysis group. On the contrary, there is very close liaison and many of the research investigations arise from difficulties first encountered by the latter group.

Another element for sustaining and encouraging analytical research is the provision of adequate funds—in addition to those provided for specific projects and requests—for general research in the field of analytical chemistry. Such funds constitute about 25% of the budget of the group, so that it is enabled to use its own initiative in investigating or developing new, broadly useful, analytical methods and techniques. When someone has an idea for a new method or sees some new technique suggested in the literature that appears applicable to some of the problems, he has the means, and the responsibility, of following through on it. The importance of this provision in its effect on the morale of the group cannot be overemphasized. It makes possible exploratory or scouting types of investigations which might often be difficult to justify on the basis of solving some specific problem, but which are so important in building a background of information which can be drawn upon for new methods and new applications. It is not necessary that these studies of new methods be limited to those pertaining directly to a current problem; frequently, it may be considered that its chief usefulness will be in connection with some future research program. Moreover, publication of such investigations is very much encouraged; during the past 5 years over 30 technical articles have been published by various members of the group, and about half of these were first presented before meetings of the AMERICAN CHEMICAL SOCIETY or of other scientific groups.

These then are what are called cornerstones for industrial analytical research. Once they are established, the specific organizational setup may not be too important.

The functioning of analytical research in one general analytical laboratory has been described as a typical example. The authors believe it represents a trend in the right direction. There are, of course, many excellent setups; superficially some of them may appear quite different, but on closer examination they are found to be very similar in the ways that really count.

TRAINING OF ANALYTICAL RESEARCH PERSONNEL

Relative to training, the authors' idea is simply that it should be designed to produce not high-grade technicians, but analytical chemists in the broadest sense of the word. A well-rounded training in the various fields of chemistry plus some background in related sciences is essential. But the emphasis should be on broadening the outlook and knowledge of the individual, rather than making him too much of a specialist. One might even say that the colleges and universities should educate; industry should

do the training. In addition to technical training, however, there are other points that seem almost as important.

Education and training in reading, writing, and speaking cannot be overemphasized. The individual must be able to assimilate what others have written and be able to organize his knowledge so that it can be clearly expressed both on paper and on foot. This is an "old chestnut," but inability along these lines is still far too common. The authors feel that a closer relationship should be developed between the English departments and the chemistry departments of the colleges and universities. The main contributions of the technical man are "the products of his mind"; his value is proportional to his ability to transmit these "products" to others.

More education—or at least some orientation—on the chemical industry as a whole is advantageous. Perhaps the universities could draw upon industry for speakers to present selected case histories—e.g., illustrating the part played by various members of the team in the course of a new development. At the same time such talks would help define the responsibilities of the research chemist, the production supervisor, and the technical salesman, as well as those of the analytical chemist upon whom the others are dependent for much of their working knowledge. Seminars, at which current articles appearing in *Chemical and Engineering News* could be discussed among the graduate students and their professors, would be helpful. For example, such articles as the recent series on "Careers in Chemistry" (*2*) would be interesting material—as would some of the articles appearing in *Fortune* magazine (*6*, *7*) that deal with the chemical industry. In short, a little "walking around knowledge" of the chemical industry, and a better picture of what is involved in earning a living in this field would indeed be worth-while assets to the new graduates.

In the case of analytical research, in particular, one can't help but feel that its requirements and opportunities in industry are not fully appreciated by many in the teaching profession. Many new graduates have stated that their professors have advised them to keep away from industrial analytical work because it leads only to routine, with no opportunity for professional advancement. It has even been questioned whether the education of the applied analytical research chemist should be on the doctorate level.

Actually industry offers many opportunities for the analytical research chemist. The status of these men is the same as that of research chemists in any other fields. Advancement, as in any job, is mainly dependent upon the individual. As has already been pointed out, however, the analytical chemist has a greater opportunity, perhaps more than any other worker in the industry, to become acquainted with all the processing, characteristics, and uses of his company's products. Such a situation is hardly one that would be calculated to minimize his value or limit his opportunities. Too, the nature of his research is usually such that it can be published promptly, thus gaining him the professional recognition of his associates in his company as well as that of other workers in the field.

A better understanding by students in chemistry of the present day role of analytical research in industry is especially important. For this they are dependent largely upon their professors. Accordingly, every means of fostering contacts and exchanges of viewpoints among teachers of analytical chemistry and those who follow it as a profession in industry must be encouraged. It is only by this means that a mutual understanding will be brought about of what industry expects in the way of training in analytical chemistry and what the universities can or cannot do in meeting these needs.

Recently, a panel discussion sponsored by the Northeastern Section of the AMERICAN CHEMICAL SOCIETY was held in Boston, Mass., on "The Education and Training of the Analytical Chemist at Mid-Century." The panel was composed of four distinguished analytical chemists—two from industry and two from the academic field. The success of this meeting is best indicated from the fact that the discussion—after the formal presentations—waxed lively for over an hour. More such meetings would be worthwhile. In calling for this better understanding, there is no intention of implying that if this could be achieved, it would start a stampede into the door of analytical research, as being a quick short cut to success. Far from it, there are many difficulties to be overcome; people to be convinced; selling to be done. All of this will require sustained effort.

Nevertheless, it is only being realistic to say that there has been a change in the past 10 years in the whole status of analytical chemistry. It is growing and developing rapidly; there are opportunities in this field. Once there is a sufficiently wide awareness of this, it can only result in attracting to the field of analytical chemistry its full share of the most promising young men. It is up to all of us both in teaching and in industry to keep the ball rolling.

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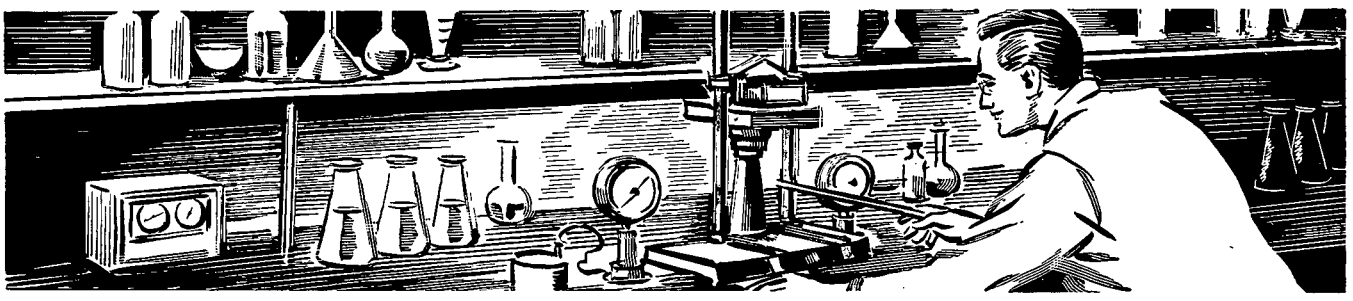

Ceric Salts in Volumetric Analysis

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The steadily increasing uses for ceric solutions in analysis and in analytical research make it desirable to review the investigations carried out in developing these solutions as volumetric reagents. The importance of related research, in finding reversible high potential indicators for ceric solutions, as well as in the commercial production of several ceric compounds from which to prepare these solutions conveniently and easily, is indicated. The wide range in oxidizing potential of the ceric-cerous system, with variation in the ceric salt used and in the acid medium for a titration, makes ceric salts unique among strong oxidizing agents. Their great stability in solution, even at considerable dilution, is also of importance. Many applications of these solutions in inorganic and organic analysis are listed.

THE editor of ANALYTICAL CHEMISTRY has said "Nothing is certain in the field of chemistry but change. Certainly the field of analytical chemistry has been no exception during the past decade, although perhaps the changes, revolutionary as they are to the analyst, have not been given the spectacular recognition accorded new developments in industrial chemistry" (*93*). These changes have occurred both in fundamental analysis and in instrumentation. It is the purpose of this paper to outline the fundamental research over a period of 23 years, in the development and use of ceric compounds in volumetric analysis, and to list a number of the applications of ceric solutions to analytical methods. Periodic reviews have described progress in this field (*45, 106, 107, 121, 138, 142, 164*).

For a long time scientists have been aware of the oxidizing property of ceric salts and occasional suggestions for their use in analytical procedures have appeared. In 1861, Lange (*79*) recognized this property of ceric sulfate and proposed it as a volumetric reagent; in 1870, Sonnenschein (*125*) recommended it instead of permanganate for the titration of ferrous ion; in 1899, Job (*64*) mentioned the stability of ceric salts in acid solution, suggested their substitution for permanganate in methods where the latter could not be used, as in the analysis of oxalochlorides, and stated that because other rare earth compounds would be without effect in any oxidation-reduction process it should be possible to prepare ceric solutions from commercial materials. In 1905, Barbieri (*6*) proposed two procedures for the determination of nitrous acid: In the first, ceric sulfate was titrated with the nitrite solution to the disappearance of the yellow color of the ceric ion, and in the second, which he stated might lead to better results, excess of ceric sulfate was added to the nitrite, and the excess was determined iodometrically. The experiments are of little value, as data are not included. Barbieri mentioned that ceric compounds are reduced in cold solution by hydrazine and hydroxylamine. He recognized also that other rare earths in ceric salt solutions caused no difficulty. In 1915, Sommer and Pincas (*124*) described a nitrometric method for determining hydrazoic acid, based on the treatment of the latter in neutral or acid solution with an excess of ceric sulfate or ammonium ceric nitrate. The nitrogen evolved was measured. More recently Martin (*85*) studied this same reaction and determined iodometrically the excess of ceric salt used in the oxidation. He stated that results accurate to within 0.1% could be obtained. Benrath and Ruland (*11*) checked the oxidizing action of ceric sulfate on a number of organic compounds such as hydrazine, tartaric acid, oxalic acid, anthracene, hydroxylamine, as well as on sodium thiosulfate, sulfurous acid, and hypophosphorous acid. Someya (*122*), in a study of the bismuthate method (*89*) for oxidizing cerium, titrated the ceric salt potentiometrically with standard ferrous sulfate, and Van Name and Fenwick (*141*) in research on bimetallic electrode systems developed graphs to describe the potentiometric titration of ceric sulfate with titanous sulfate.

Two difficulties would have been encountered immediately by earlier investigators interested in the possibilities of ceric solutions as standard oxidizing reagents. The first: there was no cheap and convenient starting material from which to prepare ceric solutions. This point will be discussed later. The second: there were no simple and accurate methods to determine end points in titrations of various reducing agents. Because of the color of the ceric ion, a visual end point might serve occasionally, but until the potentiometric method for an end point was developed any extensive and critical work in this field was impossible.

In 1925, Tomicek (*140*) reported that the oxidation potential of ceric compounds in acid solution was near that for the permanganate ion in a similar medium. Therefore, ceric salts should prove to be very strong oxidizing agents with a wide application in titrations. Moreover, it was realized that there is only one reduction product with a ceric salt—its reaction in acid medium is clear-cut—while there are a number of possible reduction products from permanganate.

EARLY METHODS FOR PREPARING AND STANDARDIZING SOLUTIONS OF CERIC SULFATE

Martin (*85*) in his work on hydrazoic acid prepared two different stock solutions of ceric sulfate and standardized them iodometrically (*21*). Solution A was made by the electrolysis of cerous sulfate in 6 *N* sulfuric acid. Solution B was obtained by diluting with water a paste of ceric oxide and concentrated sulfuric acid until the acid concentration was 2 *N*. He preferred the latter method, as it was easier to carry out.

In 1927, studies on the use of ceric salts as volumetric oxidizing agents were commenced practically simultaneously by Furman (*39*) and Willard (*151*). Either U.S.P. cerous oxalate, found by the bismuthate method (*89*) to contain 45 to 50% ceric oxide in the ignited oxide, or ceric oxide of varying purity served as the starting material in preparing solutions.

It was realized that a pure cerium compound was not necessary because interference from the other rare earths in impure cerous oxalate or ceric oxide was not to be expected. Also, the less pure the oxide of the rare earths used the more dilute the sulfuric acid required to convert it into the sulfate and the more convenient in general the procedure (*151*).

Impure oxide prepared from ignition of U.S.P. oxalate dissolved readily in sulfuric acid of specific gravity 1.3; oxide containing about 85% of ceric oxide was attacked quickly by sulfuric acid of specific gravity 1.5, while a very pure oxide had to be treated with sulfuric acid of specific gravity 1.84 to obtain the sulfate. In preparing large amounts of ceric sulfate solution, ceric oxide of about 85% purity was used. It was treated with enough sulfuric acid, specific gravity 1.5, to make the final solution 0.5 to 1 *M* in acid when diluted sufficiently to be 0.1 *N* in ceric sulfate. This acid-oxide mixture was held at 125° to 130° C. and stirred mechanically until the light brown oxide had been converted into a bright yellow paste. This paste, when cool, was added to water at room temperature. The solution had to be filtered from any unconverted ceric oxide.

Both Furman (*39*) and Willard and Young (*151*) found that the percentage of ceric oxide converted into ceric sulfate was higher for a pure oxide than for less pure material. However, concentrated sulfuric acid was required for the pure oxide, and solutions prepared from it were more expensive. To anyone wishing to prepare a ceric sulfate solution from the oxide, the procedure given above could still be recommended. But with the various ceric salts, and also ceric hydroxide, now available commercially, simpler methods for obtaining ceric salt solutions are possible, and the above procedure for preparing such a solution has become practically obsolete.

Sodium oxalate was the first primary standard suggested for use with ceric sulfate solutions (*151*). Closely agreeing results were obtained in potentiometric titrations of hot acidified oxalate solutions with the ceric salt when the volume of solution at the beginning of the titration was varied widely. Equilibrium was reached rapidly if the concentration of sulfuric acid was not too great, and if the temperature of the solution at the end of a titration was 70° C. or higher. The results were the same, whether the ceric sulfate was added slowly or rapidly during the titration. This is not the case in the titration of oxalate in a sulfuric acid medium with permanganate (*36*). The results from titrating oxalate in strong hydrochloric acid solutions, heated nearly to boiling, were the same as above, and equilibrium at the end point was reached quickly. Here, use of permanganate would be out of the question. It was found also that perchloric or acetic acid might be used instead of sulfuric or hydrochloric acid, but even a little nitric acid in the hot oxalate solution led to high results for the normality of the ceric sulfate.

As the solution is colorless in this standardization until an excess of ceric sulfate is present, it is possible to determine the end point visually in the hot solution. A blank determination should be made to find the volume of ceric sulfate required to produce the color used in an actual titration. The correction is very small.

The reverse titration, that of ceric sulfate with sodium oxalate solution, was investigated (*151*) and found to be quantitative in sulfuric, perchloric, or nitric acid medium. Hydrochloric acid had a reducing effect on the ceric sulfate in hot solution. Standard oxalic acid solution may also be used for this reverse titration (*39*). Neither of these reactions, however, would be a normal procedure in carrying out the standardization of a ceric sulfate solution.

Iodine chloride was found to catalyze the reaction between oxalate and ceric sulfate and make possible the titration of the former in hydrochloric acid solution at room temperature. Iodate or iodide also acts catalytically, but each of these requires a blank correction while iodine chloride does not, as this substance is the final form of any of these catalysts in the hydrochloric acid medium. Methylene blue also gives a very good end point in this titration in hydrochloric acid medium with iodine chloride as catalyst if prescribed conditions are followed.

A check of the above method for standardizing a ceric sulfate solution was afforded by studies made of the reaction between ferrous ion and ceric sulfate (*39, 151*). Closely agreeing results were obtained in the potentiometric titration of ferrous sulfate solutions in which the volume of solution during the titration and the amount of sulfuric acid present were varied widely. Hydrochloric or perchloric acid could replace sulfuric acid as a medium. Nitric acid caused the volume of ceric sulfate for a titration to be low.

The reverse titration, that of ceric sulfate with ferrous sulfate (*39, 122, 151*), was found to be quantitative in a sulfuric, perchloric, or nitric acid medium. A limited amount of hydrochloric acid in the ceric sulfate solution at room temperature caused no interference if the titration was made immediately.

Finally a solution of ceric sulfate was standardized by three different procedures: (1) against Bureau of Standards sodium oxalate in hot hydrochloric acid solution, (2) against Bureau of Standards sodium oxalate at room temperature in a hydrochloric acid solution containing iodine chloride as catalyst, and (3) against samples of electrolytic iron which were dissolved in hydrochloric acid and treated with a slight excess of stannous chloride, followed by mercuric chloride. The end points were determined potentiometrically. The results of the three methods were in very close agreement (*151*).

One of the first applications of ceric sulfate to be investigated was that of titrating arsenious acid (*154*), because this reaction, if quantitative, would afford another means of standardizing ceric solutions. The potentiometric titration was satisfactory in a hydrochloric acid solution at 75° to 85° C., or at room temperature with a catalyst such as iodine. Here also the most convenient form in which to use iodine was as iodine monochloride, since this would be its final form in a hydrochloric acid medium and therefore no blank correction would be required. Normalities for ceric sulfate solutions, obtained from using Bureau of Standards arsenious oxide, were found to be about 3 parts per 1000 lower than values from standardizations against sodium oxalate or electrolytic iron. Swift and Gregory studied this same titration (*134*), both with carbon tetrachloride as an indicator and with a potentiometric end point. They found either means of determining the end point accurate and showed that the slightly low results for normality reported by Willard and Young (*154*) were caused by too low a concentration of hydrochloric acid in the solution of arsenious acid being titrated. Experimental work carried out later by Willard and Young verified this point (*162*).

Ceric sulfate solutions containing sulfuric acid, or sulfuric acid with a moderate amount of nitric or perchloric acid, were found to be stable for indefinite periods and they could be boiled without change in normality (*157*). They were not sensitive to light or air.

Many methods based upon the use of ceric solutions were developed within a few years. These are referred to below under applications.

This early work has been described in considerable detail in order to bring out certain points. Ceric sulfate and potassium permanganate are of approximately equal strength as oxidizing agents in dilute solutions. What advantages has the former solution over the latter? The experimental work described above shows that ceric solutions are stable, even on boiling, that they can be used to titrate reducing agents in hot or cold hydrochloric acid medium; that they can be standardized against two readily available primary standards under a wide variety of experimental conditions; and that they can be used in hot or cold solution in excess for an oxidation, and then be back-titrated in a sulfuric, perchloric, or nitric acid medium with a standard reducing agent. Secondly, what are the disadvantages of ceric sulfate solution as compared with potassium permanganate solution? The preparation of ceric solutions from the oxide or oxalate is tedious; such solutions are relatively expensive; and only rarely can they serve as their own indicator. Obviously, if these disadvantages, which became apparent in the early work, can be eliminated, ceric salts should become more generally useful than permanganate solutions in volumetric analysis.

DEVELOPMENTS IN INDICATORS

Most of the early titrations with ceric sulfate employed potentiometric determination of end points. However, a few indicators were proposed in specific instances. Willard and Young found methylene blue satisfactory under prescribed conditions in the titration of oxalate in the presence of iodine chloride as catalyst (*151*). They used diphenylamine and diphenylbenzidine for ferrous ion obtained from a stannous chloride reduction (*152*). Knop (*72*) in 1924 had proposed diphenylamine for the titration of ferrous ion with dichromate. Its oxidation potential is 0.76 volt, a value so close to that for the ferrous-ferric system that phosphoric acid must be added before such a titration. In 1928, Rathsburg stated that trivalent antimony could be titrated with ceric salt and the end point be determined by the decolorization of methylene blue, Congo red, methyl orange, or methyl red (*98*). Furman

and Wallace tested both diphenylamine and methyl red as indicators in the titration of hydroquinone and considered the former preferable (*48*), and they proposed methyl red, erio glaucine, or erio green for titrations of ferrous ion (*49*). Swift developed methods for iodide (*132*) and arsenic (*134*) based upon the addition of iodine monochloride to a hydrochloric acid solution of the reducing agent to be titrated, and detection of the end point with carbon tetrachloride.

In 1931, Sarver and Kolthoff (*103*) prepared a sulfonic acid derivative of diphenylamine. This new indicator had a slightly higher oxidation potential than diphenylamine (0.84 volt as compared with 0.76 volt), was soluble in water, and could be used in solutions containing tungstates. Here also in titrating ferrous ion, phosphoric acid had to be added to remove ferric ion, as the oxidation potential of the ferrous-ferric system was still so close to that of the indicator system that the ferric ion had an oxidizing action on the indicator.

In 1931, Kunz (*77*) made the first careful measurement of the potential of the cerous-ceric electrode. He found it to have a value at 25° C. of 1.44 volts in 1.0 formal sulfuric acid, in comparison with 1.48 volts for the molal potential of the permanganate-manganous system in the same acid medium. Therefore it was apparent that neither diphenylamine nor its sulfonic acid derivative was of sufficiently high potential to be adapted to titrations with either of these oxidizing solutions.

A reversible oxidation-reduction indicator of sufficiently high potential to serve generally in titrations with ceric salts was badly needed. Such an indicator should have a potential higher than 0.9 volt if phosphoric acid or other complex-forming reagent were to be omitted in titrations of ferrous ion, and its potential should be well over 1.0 volt for the broadest possible use in titrations with ceric sulfate. In 1931, Walden, Hammett, and Chapman (*145*) announced that ferrous *o*-phenanthroline complex ion, prepared originally by Blau (*18*) and now called ferroin, could serve as a reversible oxidation-reduction indicator of high potential. In its reduced form it was deep red in color and in its oxidized form was pale blue. They reported its molar oxidation potential to be 1.14 volts (as compared with 0.84 volt for diphenylamine sulfonic acid), and stated that the reduced form was stable for several hours in a strong acid solution at room temperature and that the ferric complex was resistant to acids and to action by permanganate, ceric, or dichromate ions in acid solution. The amount of indicator solution required for a titration was 1 drop of 0.025 *M* solution. A more detailed report of their study of the preparation and properties of this new indicator was published in 1933 (*146*). In titrations with 0.1 *N* oxidizing agent they found no indicator correction necessary. Only with more dilute oxidizing solutions should a blank correction be made. The authors stated that an aqueous 0.025 *M* solution of the *o*-phenanthroline ferrous ion (also referred to as 1,10-phenanthroline ferrous ion) showed no evidence of decomposition after a year. Their experiments with 2,2′-bipyridine ferrous ion, also described first by Blau (*18*), showed it to be less satisfactory for indicator purposes than ferroin because of its more rapid decomposition in acid solution. Recently Hume and Kolthoff (*63*) have found formal oxidation potential of ferrous-*o*-phenanthroline complex ion—1.06 volts.

In 1934, Hammett, Walden, and Edmonds (*54*) extended their study of high potential indicators by preparing and checking certain derivatives of phenanthroline and diphenylamine. Nitrophenanthroline ferrous ion, now called nitroferroin, was found to have a potential of 1.25 volts; it was, moreover, even more stable toward acids than *o*-phenanthroline ferrous ion, and appeared not to be affected by vanadic acid in 1 *M* sulfuric acid; the latter indicator was oxidized in such a solution. When this nitro derivative was used as an indicator in the titration of ferrous ion with ceric sulfate, the end point was not satisfactory. A measurable excess, though small, of the ceric solution was required to oxidize the indicator—proof that the potential of this indicator was too high for satisfactory results with ceric sulfate. (Very important uses for this indicator are given below). A second indicator of interest which they prepared and checked was *p*-nitrodiphenylamine. Its oxidation potential was about 0.3 volt higher than that of diphenylamine; like the latter the nitro derivative was not a reversible indicator. It gave an excellent end point in the titration of ferrous ion with ceric sulfate. When a second nitro group was introduced into diphenylamine, an indicator of still higher potential was formed. Various amino derivatives of diphenylamine were also checked, and from this study of oxidation potentials and indicator properties of these new substances, a number of indicators with potential values different from those of indicators in use at the time were obtained.

Other oxidation-reduction indicators of high potential were described during this period. Among those of special interest for titrations with ceric sulfate the following may be mentioned. *N*-phenanthranilic acid (*o*-diphenylamine carboxylic acid) was found by Syrokomsky and Stiepin (*135*) to have an oxidation potential of 1.08 volts. It was colorless in reduced form and pink in oxidized form. The latter form was stable and reversible. When used as an indicator in titrations of ferrous ion, the presence of phosphoric acid was not necessary. The authors recommended this indicator for titrations with ceric sulfate; the color changes were very sharp and indicator corrections negligible. They pointed out also that the indicator had an oxidation potential near that of ferrous-*o*-phenanthroline complex ion, and was to be preferred to the latter in ease of preparation and cost. The 2,2′-bipyridine ruthenous complex ion was prepared by Burstall (*23*) and examined for use as an indicator by Steigman, Birnbaum, and Edmonds (*128*). It was found to be a reversible system, in which at indicator dilutions the ruthenous complex ion was yellow and the corresponding ruthenic ion colorless. Both the reduced and oxidized forms were more stable in acid solution than the corresponding iron complexes of 2,2′-bipyridine. The molar oxidation potential of this indicator was 1.33 volts. Therefore one would not expect that it could be used in titrations with ceric sulfate, and such was found to be the case. Later Hume and Kolthoff (*63*) obtained a value of 1.25 volts for the formal oxidation potential of the ruthenous-ruthenic 2,2′-bipyridine system, and very recently Brandt and Smith (*20*) have verified this value.

Improved syntheses for *o*-phenanthroline (*116*) and for 5-nitro-1,10-phenanthroline (*110*) were reported and a number of 5(6) derivatives of 1,10-phenanthroline were prepared (*100*). The possibility of using 2,2′-bipyridine ferrous ion was investigated (*24*). This indicator has a formal oxidation potential of 0.97 volt and has been noted earlier to be somewhat less stable in its oxidized form than is *o*-phenanthroline. It is, however, much less expensive, and would be desirable in titrations of ferrous ion with ceric sulfate. The authors show that it can be used to determine iron in sulfuric acid solution after passage through a Jones reductor, or in a hydrochloric acid solution after passage through a Walden reductor. The 5,6-dimethyl-1,10-phenanthroline ferrous ion was studied (*109*). It was found to have an oxidation potential of 0.97 volt in 1 *F* acid and it showed a high degree of stability in both its oxidized and reduced forms. This indicator with its lower oxidation potential than *o*-phenanthroline ferrous ion was found very satisfactory in titrations of ferrous ion with dichromate. Very recently a report on the study of a number of polysubstituted (methyl) 1,10-phenanthrolines has appeared (*20*) in which are listed indicators with oxidation potentials covering a range from approximately 0.8 to 1.0 volt.

While reversible oxidation-reduction indicators covering a wide range in oxidation potential were being prepared and examined, new cerium compounds for use as volumetric oxidizing agents were being made, and new concepts of oxidation with ceric compounds were being formulated.

PREPARATION OF CERIC SOLUTIONS

In the first few years of experimentation with ceric salts, the solutions were invariably prepared by reaction between

ceric oxide and sulfuric acid to form solid ceric sulfate. After this solid was dissolved in dilute sulfuric acid solution, a filtration was necessary to remove unchanged ceric oxide. Such a procedure was slow and was bound to discourage individuals from experimenting with ceric solutions and using them in analyses. Simpler methods for preparing such solutions were imperative before one could look forward to their more general use. Shortly ceric ammonium sulfate, of composition $2(NH_4)_2SO_4 . Ce(SO_4)_2 . 2H_2O$, was made available in limited quantities by O. T. Coffelt. This salt, which dissolved easily in warm, dilute sulfuric acid, provided a rapid and convenient means of preparing ceric solutions.

One chemical supply house had already listed among its stock items ceric sulfate solutions, of both approximate and standard strength, especially for the convenience of the smaller consumer who might wish to experiment with this oxidizing agent. In 1933, Smith (*107*) published material on new methods of preparing ceric salts from cerous compounds.

Hydrated cerous oxalate, impure, was the starting material. This was dissolved in concentrated nitric acid. Then 70 to 72% perchloric acid was added and the mixture was concentrated to fumes of the latter. One would expect the cerous salt to be oxidized at this point, but actually it was reduced as rapidly as formed because of the formation of hydrogen peroxide (*108*), this reaction being catalyzed by the cerium in the solution. If 70 to 80% sulfuric acid was added to this cerous perchlorate-perchloric acid mixture, and the material heated at the proper temperature, ceric sulfate, very insoluble in these mixed acids, was quantitatively formed. This solid was separated from the acids by centrifuging, and any perchloric acid remaining in the precipitate was washed out with portions of 75 to 80% sulfuric acid. The residue, moist with sulfuric acid, dissolved readily to give ceric sulfate solution. If the solid was finally washed with water to remove excess acid, and dried at 190° C. to remove any remaining water and sulfuric acid, a yellow ceric sulfate was obtained which, after pulverizing, dissolved in warm, dilute sulfuric acid to give a clear solution of ceric sulfate.

Solid ceric ammonium sulfate was also prepared by adding to a dilute sulfuric acid solution of ceric sulfate the correct amount of ammonium sulfate and concentrating the solution. Orange crystals of ceric ammonium sulfate separated. This latter salt was more readily soluble in dilute sulfuric acid than the anhydrous ceric sulfate, but more of it was required in preparing a ceric solution.

Thus two ceric salts became available through supply houses early in the 1930's. This first work on the commercial preparation of ceric salts gave impetus to the preparation and study of other ceric compounds.

In 1936, Smith, Sullivan, and Frank (*120*) proposed the complex salt, ammonium hexanitratocerate, $(NH_4)_2Ce(NO_3)_6$, as a standard of reference in oxidimetry.

In preparing it they started with a low-grade thorium-free ceric oxide, and in the first crystallization of their final product obtained ammonium hexanitratocerate, which was 99.5% pure. When this was recrystallized from concentrated nitric acid containing an excess of ammonium nitrate, an 80% yield of pure salt was obtained. This salt dissolved readily in dilute sulfuric acid to give a solution stable even when digested for 1 to 2 hours at 100° C. It could be dried at 110° C. It was soluble in water without hydrolysis, as well as in sulfuric, nitric, perchloric, and hydrochloric acids. Pure ceric sulfate or cerous chloride could be prepared from it by digestion with the corresponding acid in excess. The authors considered that this material was a complex, not a double, salt, and that it ionized as follows:

$$(NH_4)_2Ce(NO_3)_6 \longrightarrow 2NH_4^+ + Ce(NO_3)_6^{--}$$

As early as 1901, Meyer and Jacoby (*90*) from a study of the properties of this same salt believed that the cerium was in the anion—that the salt dissociated into NH_4^+ and $Ce(NO_3)_6^{--}$ ions. Jones and Soper (*65*) had very recently (1935) studied the nature of the ceric sulfates. These authors stated that in solutions of ceric sulfate or of the double ceric sulfates, $M_2Ce(SO_4)_4$, they had always found cerium to exist as an anion. There was no evidence of any positive ceric ions in these solutions. They also described a number of ionic migration experiments which they carried out on sulfuric acid solutions of ceric sulfate, of the potassium and sodium double salts, and of a mixture of ceric sulfate with lithium sulfate, in all of which the colored ion containing cerium migrated to the anode.

Measurements of Oxidation Potentials of Cerous-Ceric Systems. Early measurements of oxidation potentials on cerous-ceric salts in nitric and in sulfuric acid solution had been made by Bauer and Glaessner (*8*). Kunz (*77*) more recently had found the single electrode potential of the cerous-ceric system in 1 *F* sulfuric acid to be 1.44 volts; Noyes and Garner (*96*) obtained the value 1.610 volts for the cerous-ceric potential in nitric acid at 25° C., between concentrations of 0.5 and 2.0 *F* in nitric acid; and Sherrill, King, and Spooner (*105*) reported a value of 1.640 to 1.731 volts for the cerous-ceric perchlorate system in concentrations of perchloric acid from 0.2 to 2.4 *F* by weight.

In 1938, Smith and Getz (*117*) published the results of some very interesting work. These authors pointed out that titrations using ceric salts had been made, up to this time, in either a sulfuric or hydrochloric acid solution of the reducing agent, and that ceric sulfate or ceric ammonium sulfate had served as the oxidizing solution. In the first experiments described by Willard and Young (*151*), it was stated that perchloric acid in the reducing solution or nitric or perchloric acid in a ceric sulfate solution being titrated with a reducing agent caused no difficulty. Smith, Sullivan, and Frank (*120*) had demonstrated the great stability of solutions of ammonium hexanitratocerate in dilute sulfuric acid, and had predicted that the nitrate ion in such solutions would cause no interference in most cases. Smith and Getz proposed to determine approximate values for the single electrode potential of the cerous-ceric system in perchloric and hydrochloric acid solutions as well as in nitric and sulfuric acid, and to find out in what way these values varied in the different acid media with change in concentration of acid.

Pure cerous chloride, sulfate, nitrate, and perchlorate were prepared. These solutions were oxidized electrolytically in a diaphragm cell by the method of Hengstenberger (*60*) to the corresponding ceric compounds. Then solutions 0.025 *N* in trivalent and tetravalent cerium, and from 1 *N* to 8 *N* in free acid, were prepared and the single electrode potential for the cerous-ceric system in each solution determined. The results were as follows:

In $HClO_4$ solution of acidity 1 to 8*N*, potential varied from 1.70 to 1.87 volts
In HNO_3 solution of acidity 1 to 8*N*, potential varied from 1.61 to 1.56 volts
In H_2SO_4 solution of acidity 1 to 8*N*, potential varied from 1.44 to 1.42 volts
In HCl solution of acidity 1*N*, potential equaled 1.28 volts

Thus in 1 *N* acid these potentials vary from 1.70 volts in perchloric acid to 1.28 volts in hydrochloric acid. Moreover, as the concentration of the acid increases in the cases of nitric or sulfuric acid solutions the potentials show a drop in the range of 4 *N* to 8 *N*. But with perchloric acid solutions, the potential increases steadily as the concentration of acid is increased.

In earlier work with ceric solutions the fundamental equation had been assumed to be: $Ce^{++++} + 1e = Ce^{+++}$. It is difficult to account for the change in the single electrode potential in the different acid media or in solutions in a given acid at different concentrations on the basis of this simple equation. Smith and Getz also found that the higher single electrode potential in perchloric or nitric acid solutions could be lowered to approximately that in sulfuric acid by adding enough of the latter to be equivalent to the perchloric or nitric acid present. And the reverse process was also true: The single electrode potential in sulfuric acid solution could be markedly increased by the addition of an equivalent amount of perchloric or nitric acid. The authors explained these facts on the basis of complex-ion formation. They considered that in these solutions ceric cerium was present mainly as $Ce(ClO_4)_6^{--}$, $Ce(NO_3)_6^{--}$, $Ce(SO_4)_3^{--}$, and $CeCl_6^{--}$.

The data of Smith and Getz for the ceric-cerous potential in the four different acid media indicate that complex-ion formation may be an important factor in sulfuric, nitric, and possibly hydrochloric acid solutions, but that a different interpretation is required of the values obtained in perchloric acid solutions. The steady increase in potential of the ceric-cerous half-cell with in-

crease in perchloric acid concentration cannot be accounted for, as they suggest, by complex-ion formation. Solutions of the sulfates have been studied most frequently in the past, and complex-ion formation has been proposed for them. It may be more accurate, therefore, to use the term "cerate oxidimetry" rather than "ceric oxidimetry." But it is very desirable that further studies of properties of ceric solutions should be undertaken to clear up uncertainties and contradictions in interpretations of the form of cerium in these oxidizing solutions.

Smith and Getz have demonstrated that the perchloratocerate and nitratocerate ions are especially strong oxidizing agents. The latter was available already in the form of solid ammonium hexanitratocerate, but the former was available only as a solution from electrolytic oxidation of cerous perchlorate, not a convenient form for its general use. The authors therefore carried out experiments to determine whether solutions of ammonium hexanitratocerate in perchloric acid would provide a potential nearly as high as that from the hexaperchloratocerate ion in perchloric acid. This substitution was found possible with only a slight loss in oxidizing power. The availability of this very strong oxidizing solution (prepared by dissolving ammonium hexanitratocerate in 72% perchloric acid and diluting to the proper volume) opened up new possibilities in differential oxidations and suggested alterations in procedures already in use. Moreover, an indicator described earlier, nitro-*o*-phenanthroline ferrous complex, found to have too high an oxidation potential for use with ceric sulfate, should be ideally adapted for use in titrations with nitratocerate and perchloratocerate solutions. Such has been found to be the case.

In 1940, a simpler method was described for the electrolytic oxidation of cerous sulfate, nitrate, and perchlorate in sulfuric, nitric, and perchloric acid solutions to the corresponding ceric acids (*114*). In earlier experiments a diaphragm cell had been used (*60, 117*) but this work proved the diaphragm unnecessary, as was to be expected if the oxidized cerium was in a complex negative ion. The formulas of these acids and of the corresponding hexachloroceric acid were given as $H_2Ce(ClO_4)_6$, $H_2Ce(NO_3)_6$, $H_2Ce(SO_4)_3$ or $H_4Ce(SO_4)_4$, and H_2CeCl_6. This study provided the first convenient means of preparing solutions of hexaperchloratoceric acid in the laboratory or commercially.

Ammonium hexanitratocerate was proposed in 1936 as a standard of reference in oxidimetry (*120*), but a detailed study of its properties was not made at that time. Smith, the senior author of that article, has published very recently with Fly (*113*) results of such a study. These authors recommend unqualifiedly the use of ammonium hexanitratocerate as a primary standard. The chemically pure salt, available through supply houses, should be dried at 85° to 87° C. If dried at 110° C., as suggested earlier, there is a small loss in weight. The authors give directions for dissolving weighed samples of the salt in either perchloric or sulfuric acid and for diluting such solutions to a definite volume. Also, weighed samples may be converted into ceric hydroxide by precipitation with excess ammonia, and the precipitate be dissolved in warm, dilute sulfuric acid. This solution, if diluted to a definite volume, provides a solution of standard sulfatoceric acid free from ammonium and nitrate ions.

STABILITY OF SOLUTIONS

Studies have been published on this subject (*39, 119, 157*), and much descriptive material is found on the checking of the stability of cerate solutions. One-tenth normal sulfatocerate solutions in sulfuric acid, whether prepared from ceric hydroxide, ceric sulfate (tetrasulfatoceric acid), or ammonium hexanitratocerate, are extremely stable and may be heated at 100° C. for a considerable time without change in concentration. Moreover, moderate amounts of nitric or perchloric acid in these solutions containing free sulfuric acid do not lessen their stability even at 100° C. Such solutions, therefore, far surpass permanganate solutions of the same normality in stability.

Solutions prepared by dissolving ammonium hexanitratocerate in nitric or perchloric acid have a considerably higher oxidation potential than sulfuric acid solutions of this solute, and would be expected to be much less stable. Smith and Getz (*119*) checked the stability of thirteen solutions of this solute in various concentrations of nitric or perchloric acid. These solutions, from 0.008 to 0.1 *N* in oxidizing content, were stored in diffused light or in the dark for extended periods of time (up to 8 months) and samples of them were titrated periodically for normality. Experimental results may be summarized as follows:

A small but detectable decomposition was evident in solutions stored in diffused light rather than in the dark; the solutions from 1 to 3 *M* in nitric or perchloric acid showed the greatest stability; the stability of all the solutions increased with time; the presence of appreciable amounts of other rare earths did not affect the stability of the solutions. The following data are representative: A 0.1 *N* solution of purified ammonium hexanitratocerate, 2 *M* in perchloric acid, after storage in the dark for 19 days decreased in normality by 3 parts in 1000; a 0.05 *N* solution of the commercial solute, 3.0 *M* in nitric acid, after storage in the dark for 30 days decreased in normality by 7 parts in 1000. Solutions of hexaperchloratoceric acid in perchloric acid were also included in this study. One of these, 0.05 *N* and 3.0 *M* in perchloric acid, after being stored in the dark for 15 days, decreased in normality by 6 parts in 1000. Therefore such solutions could be used a number of days between standardizations.

When more dilute cerate solutions are considered, their stability as compared with permanganate solutions of equal normality becomes more pronounced. The former solutions in 0.001 *N* concentration, if allowed to stand for a few days before being standardized, show very satisfactory stability (*66, 70*). This is one reason for the increasing use of cerate solutions in micromethods.

PREPARATION OF SOLUTIONS

Ammonium hexanitratocerate, available through supply houses, is one of the most desirable materials for this purpose. The proper amount may be added to sufficient perchloric acid, 72%, to give after dilution a solution from 1 *N* to 8 *N* in perchloric acid. The salt does not dissolve in the concentrated perchloric acid, but the two must first be thoroughly mixed, and then be diluted very slowly to the final volume while being stirred continually. If the salt is added directly to dilute perchloric acid, a solution is obtained but it does not remain clear. Such a solution will be the equivalent of a perchloratoceric acid solution in its potential. Depending on its normality in perchloric acid, its potential will vary from approximately 1.7 volts to well above 1.8 volts. By a similar procedure ammonium hexanitratocerate may be stirred with sufficient concentrated sulfuric acid to provide a solution 0.5 to 1.0 *M* in sulfuric acid after dilution. The mixture is then diluted very slowly while being stirred continually, and a solution equivalent in properties to one of ammonium sulfatocerate is obtained. In preparing a solution of hexanitratoceric acid in nitric acid the salt may be dissolved directly in dilute nitric acid (*106*). These solutions will contain the ammonium ion and the first two the nitrate ion as foreign ions, but rarely will these ions cause interference. A second very desirable starting material is ceric hydroxide which dissolves readily in hot dilute sulfuric acid to form sulfato ceric acid. This is the most convenient method for preparing such a solution. Directions are given in a recent article by Cagle and Smith (*24*). With these two solids available, the ammonium nitratocerate and ceric hydroxide, all cerate solutions ordinarily desired may be quickly made.

There are two other convenient materials from which to prepare solutions. Sulfatoceric acid, $H_2Ce(SO_4)_3$, solution, approximately 0.5 *N* and 1 *M* in sulfuric acid, may be purchased. Measured volumes of this, when diluted to 5 or 10 times their original volume with 0.5 or 1.0 *M* sulfuric acid, will provide solutions 0.1 or 0.05 *N* in oxidizing strength. Similarly, perchloratoceric acid, $H_2Ce(ClO_4)_6$, solution, approximately 0.5 *N* and 6 *M* in

perchloric acid, is available commercially, and may be diluted with perchloric acid to provide solutions of the desired normality and 1 to 8 *M* in perchloric acid.

Two other solids on the market are ammonium tetrasulfatocerate, $(NH_4)_4Ce(SO_4)_4 \cdot 2H_2O$, and tetrasulfatoceric acid, $H_4Ce(SO_4)_4$. These are not so desirable in the preparation of solutions as the materials already mentioned. The first, though readily soluble, is more expensive, and the second does not always dissolve completely in sulfuric acid.

STANDARDIZATION OF SOLUTIONS

Solutions of sulfatoceric acid may be standardized in a number of ways:

Against arsenious oxide in a sulfuric acid medium at room temperature with osmium tetroxide as catalyst (*52*) and ferroin as indicator (*149*).

Against sodium oxalate in hydrochloric acid solution with iodine chloride as catalyst and ferroin as indicator. The entire titration is made between 45° and 50° C. (*149, 162*).

Against arsenious oxide in a hydrochloric acid solution with iodine chloride as catalyst and ferroin as indicator. The major part of the titration is made at room temperature. When near the end point the solution is heated to 50° C. and the titration completed by the slow addition of the ceric solution (*162*).

Against sodium oxalate in sulfuric acid medium. A measured excess of sulfatoceric acid is added and the solution is heated to 50° C. and held at that temperature for 5 minutes. After cooling, ferroin is added as indicator and the solution is back-titrated with ferrous sulfate solution. In another titration a measured volume of sulfatoceric acid is reduced with the same ferrous sulfate solution, with ferroin as indicator (*106*).

Against electrolytic iron (*149*).

Other materials against which cerate solutions have been standardized are potassium ferrocyanide (*123, 142*), Mohr's salt (*39, 49*), and arsenious oxide in hydrochloric acid containing iodine chloride as catalyst and carbon tetrachloride for determining the end point (*134*). Only the last named material is a primary standard. Results obtained from its use in this method are accurate, but the procedure is somewhat troublesome.

Nitratocerate and perchloratocerate solutions may be standardized conveniently in either of the following ways:

Against sodium oxalate in perchloric acid solution. Nitroferroin is added as indicator and the titration is carried out at room temperature (*118*).

Against arsenious oxide in perchloric acid solution. Osmium tetroxide is added as catalyst (*52*), nitroferroin as indicator, and the titration is carried out at room temperature (*118*).

CONCLUSIONS

This brief outline of research in the development of cerate solutions as standard volumetric oxidizing agents illustrates the necessity of a many-sided approach to any larger problem. Such solutions would not have attained their present importance and usefulness if there had not been made available both reversible, high potential indicators and several ceric compounds from which solutions could be conveniently and easily prepared.

The present picture might be summarized as follows: Sulfatoceric acid solution in titrations of reducing agents in hydrochloric acid medium provides an oxidizing potential approximating that of dichromate solution; the same cerate solution in titrations in sulfuric acid medium provides an oxidizing potential approximating that of permanganate solution; and both nitrato and perchloratocerate solutions when used in perchloric acid medium show considerably higher oxidation potentials. Therefore it can scarcely be said that permanganate and cerate solutions are equally useful as strong oxidizing agents. Cerate salts more than cover the range in potential provided by both dichromate and permanganate; they are, moreover, to be preferred to the former because of their colorless reduction product, and to the latter because of their much greater stability in hot solutions and at considerable dilution.

Why is it that cerate solutions have not attained as wide a use as might be expected? For one reason, because of the inertia always shown on occasion in trying something different when something that appears satisfactory is already available. But, most important, because authors of textbooks in quantitative analysis and teachers of that subject have not waked up to the fact that they are behind the times in discussing in detail permanganate as an oxidizing agent and then disposing of cerate solutions by saying "they may be substituted for permanganate as a rule."

In a recent article (*30*) the following statements were made: "One of the most serviceable fundamental bases for research in analytical chemistry is thorough indoctrination in the methods, techniques, and approaches of so-called classical gravimetric and titrimetric analysis. A comprehensive training in these fields gives one the basic attitude necessary for the most expeditious solution of analytical problems." And later, "The analytical chemist should be taught principles, not methods; he should learn 'instrumentation,' not 'instrumental analysis.'" The author of this review believes that a chapter such as "A Comparative Study of Cerate, Permanganate, and Dichromate Ions as Oxidizing Agents in Volumetric Analysis" should be a part of a modern textbook in quantitative analysis.

APPLICATIONS

The following applications do not represent a complete bibliography to date of methods employing a cerate solution, but they serve to indicate the wide uses already made of this oxidizing agent.

Aluminum has been determined (*86*) by a method similar to one proposed for magnesium in biological material (*94*). The precipitate obtained with 8-quinolinol from a solution containing acetic acid and acetate was dissolved in perchloric acid and the 8-quinolinol oxidized in hot solution with a measured excess of standard cerate solution. The unused cerate was titrated with ferrous sulfate, with ferroin as indicator. As the oxidation of the oxyquinoline is an empirical process, the aluminum equivalent of the cerate solution must be determined against potassium alum by the same process. This method is said to be especially suited to microdeterminations of aluminum.

Antimony as antimonous chloride has been titrated with ceric sulfate at room temperature, with iodine chloride as catalyst. The end point was determined potentiometrically or with methylene blue added near the end of the titration (*154*). Ferroin may also be used as indicator (*162*). In the presence of limited amounts of arsenic, this titration may be made successfully at room temperature with a catalyst, if the solution contains 30 to 50% by volume of concentrated hydrochloric acid at the beginning of the titration (*41, 97, 98*). The end point is determined potentiometrically or with methyl orange, methyl red, methylene blue, or Congo red (*98*). Use of methyl orange has been stressed (*41*).

Arsenic in hydrochloric acid solution may be titrated potentiometrically with cerate at 75° to 85° C., or at room temperature in the presence of iodine chloride as catalyst (*134, 154, 162*). With iodine chloride in the hydrochloric acid solution, ferroin may serve as indicator if the solution is warmed to 50° C. near the end of the titration (*162*), or a globule of an immiscible organic solvent, as chloroform or carbon tetrachloride, may be added and the end point determined by the disappearance of the color of iodine in the organic solvent (*134*). The titration of arsenious acid in sulfuric acid medium with cerate solution, in the presence of osmium tetroxide as catalyst and ferroin as indicator, is rapid and accurate (*52*). If antimony is present with arsenic, the former is titrated first in strong hydrochloric acid medium (see antimony), followed after dilution of the solution by titration of arsenious acid by one of the methods given above. This procedure applies only if the ratio of antimony to arsenic is large.

Titration at 50° C. of arsenious acid in hydrochloric acid solu-

tion containing iodine chloride as catalyst and ferroin as indicator has been employed for arsenic in Paris green and in lead arsenate after reduction of arsenic with hydrazine and distillation of the arsenious chloride (*87*). The authors prefer this procedure to an iodometric method because of the great stability of both the oxidizing and indicator solutions.

A method for micro amounts of arsenic (2.0 to 0.1 mg.) has been described, based upon reduction of the arsenic from its tri- or pentavalent form to the element by calcium hypophosphite in approximately 6 *N* hydrochloric acid. The product was filtered and the arsenic dissolved in a measured excess of cerate solution (0.004 *N* to 0.005 *N*). After addition of osmium tetroxide as catalyst and ferroin as indicator, the excess oxidizing agent was titrated with 0.005 *N* arsenite. Tin, antimony, lead, copper, iron, and bismuth do not interfere. One milligram of arsenic was determined with an accuracy of 0.5%; 0.1 mg. with an accuracy of 1 or 2% (*75*).

The volumetric microdetermination of arsenic in a 2*F* perchloric acid solution has been checked. Osmium tetroxide was used as catalyst and a 0.0005 *M* solution of nitroferroin as indicator, and titration made with 0.001 *N* perchlorato ceric acid. Data for a number of titrations of arsenious oxide (0.15 to 0.27 mg.) were given. The average error was 0.57% (*115*).

Calcium has been determined indirectly by dissolving a precipitate of calcium oxalate in hydrochloric acid and titrating the oxalic acid in hot solution either potentiometrically or to a visual end point with ceric sulfate (*151*). The titration was also made at 50° C. with iodine chloride as catalyst and ferroin as indicator (*162*). Variations of this procedure have been used in the microdetermination of calcium (*29, 66, 68, 70, 74, 80, 81, 83, 102*). Some of these investigators have dissolved the oxalate in perchloric acid and titrated the solution at room temperature with nitrato or perchlorato cerate in perchloric acid. Ferroin, nitroferroin, and setopaline C have been used as indicators.

In another micromethod, calcium has been precipitated with a measured excess of 0.001 *N* potassium ferrocyanide in a solution basic to methyl red and containing 50% by volume of 96% ethyl alcohol. The precipitate was dissolved in sulfuric acid and the ferrocyanide titrated with ceric sulfate, with ferroin as indicator (*35*).

Chromium may be determined by oxidation in hot solution with an excess of ceric salt. Three procedures have been proposed: (A) use of measured excess of standard ceric solution, the excess being determined in the presence of chromic acid by differential titration with sodium oxalate or sodium nitrite; (B) oxidation with excess ceric sulfate, followed by addition first of nitrite in slight excess to destroy ceric salt, then by urea to reduce the nitrite, and titration of the chromic acid with standard ferrous sulfate and (C) the same as B except that sodium azide was added at 35° to 40° C. to destroy the excess ceric salt. With nitrite the excess must be slight and the time of its action short, but with azide a large excess, even if present for some time, has no effect on the chromic acid. End points were determined potentiometrically. Iron and large amounts of manganese caused no interference. Vanadium, if present, was determined with the chromium (*156*).

Method A, with the use of standard sodium nitrite in the final potentiometric titration, has been adapted to the determination of trivalent chromium in chromium plating baths and in chromic acid (*163*).

Copper. The precipitate of cuprous oxide obtained from the action of alkaline copper sulfate on reducing sugars may be dissolved in a measured excess of standard cerio sulfate, and back-titration made with ferrous sulfate, with ferroin as indicator. Results were reported to be better than those by the permanganate and dichromate methods (*126*). This method for cuprous oxide has been adapted to the determination of copper in Paris green and in ores (*88*).

It has been found that cupric ion in 2 *M* hydrochloric acid solution at room temperature is quantitatively reduced to the cuprous form by passage through the silver reductor. With an excess of ferric alum solution in the filtering flask, ferrous ion equivalent to the cuprous ion is formed and may be titrated with standard cerate, with ferroin as indicator. Nitric acid, zinc, stannic tin, arsenate, bismuth, and cadmium do not interfere. Iron, molybdenum, uranium, and vanadium must be absent (*15*). This procedure has been applied successfully to copper in brass (*15*).

Electrolytic copper in micro quantities may be dissolved and oxidized by a measured excess of standard cerate in 2 *N* sulfuric acid if chloride ion is present. The excess oxidizing agent is then titrated with ferrous sulfate solution, with ferroin as indicator. For 0.2 to 1.2 mg. of copper the error was 1% or less (*19*).

Methods for metallic copper and cuprous oxide in commercial cuprous oxide pigments and for metallic copper in cuprous oxide–cupric oxide mixtures have been described (*4*). Selective solvents were used for cuprous oxide, and the metallic copper remaining alone or with cupric oxide was dissolved in acid ferric chloride and the ferrous ion formed titrated with ceric sulfate. The total reducing power of a mixture of copper and cuprous oxide was determined in the same way.

Solid cuprous chloride has been analyzed by adding to a weighed sample an excess of ferric ammonium sulfate solution, 3 *M* in sulfuric acid. After solution of the sample, ferroin was added and the ferrous ion titrated with cerate solution (*59*).

Ferrocyanide ion has been titrated with ceric sulfate in dilute hydrochloric or sulfuric acid medium, either potentiometrically or to a visual end point consisting of the disappearance of a greenish color due to ferric ferrocyanide if traces of ferric iron are present (*43*). Ferroin gives an excellent end point in this titration (*162*), and diphenylamine sodium sulfonate has proved satisfactory (*12*). Other studies of this reaction have made use of a potentiometric end point (*3, 123*). The titration of ferrocyanide in the presence of arsenious acid, with ferroin as indicator, has been reported (*78*).

Hydrazine has been determined by oxidation with excess alkaline ferricyanide solution, followed by titration of the ferrocyanide with ceric ammonium sulfate, after acidifying with hydrochloric acid. The end point was determined either by the disappearance of the green color in the solution and the appearance of a brownish color, or more clearly by the addition of a few drops of ferric chloride when within a few milliliters of the end point (*27*). The amount of ferricyanide used has to be controlled rather carefully: If the excess is slight, oxidation of the hydrazine may not be quantitative; if too large, the end point in the titration is difficult to determine.

Hydrazoic Acid and Azides have been oxidized in neutral or acid medium by an excess of cerate solution. The nitrogen formed has been measured (*124*). If a definite excess of standard cerate solution is used for the oxidation, the excess may be determined iodometrically with results accurate to within 0.1% (*85*).

More recently lead azide has been oxidized by a measured excess of standard nitratocerate solution in nitric acid. The excess was titrated with ferrous sulfate, with ferroin as indicator. Results from this method are reported to be only slightly less reproducible than those from precipitation of the azide as silver azide. Moreover, the procedure is easy to carry out and more rapid than either of the others (*1*).

Hydrogen Peroxide has been titrated potentiometrically in sulfuric acid solution with ceric sulfate (*3*). A detailed study of this titration showed that it could be made in hydrochloric, acetic, nitric, or sulfuric acid solutions of moderate concentration. The reaction was rapid in the presence of either of the first two acids, somewhat slower in nitric acid, and very slow in sulfuric acid, especially in the region of the end point (*47*). Ferroin has been found satisfactory for a visual end point (*162*). This titration has been adapted to hydrogen peroxide in the presence of Caro's acid (*13*). In a review of methods for determining active

oxygen in commercial peroxygen compounds, titration with ceric solution, with ferroin as indicator, was considered desirable for solutions containing hydrochloric acid or organic matter (*99*).

This titration has been used in the indirect analysis of lead peroxide for available oxygen. In one procedure the sample was treated with a measured excess of standard hydrogen peroxide in nitric acid solution, and the excess titrated potentiometrically with ceric sulfate (*47*); in a second procedure, the peroxide was decomposed by a known excess of oxalate in perchloric acid solution, and the excess oxalic acid titrated with ceric sulfate (*92*). The latter method would appear to be preferable.

Iodide in a sulfuric acid solution may be titrated potentiometrically with ceric sulfate. Iodine is formed. Moderate amounts of bromide cause no interference. The same titration, if made in a hydrochloric acid medium, leads to the formation of iodine chloride (*153*). In the latter titration the end point may also be determined by the disappearance of the color of iodine in a globule of an immiscible solvent, as carbon tetrachloride (*132*). Iodide in a sulfuric acid solution containing acetone may be titrated with ceric sulfate, with ferroin as indicator. The iodine liberated reacts with acetone to form iodoacetone. The method is stated to be accurate in the presence of limited amounts of bromide or chloride ion (*82*). Iodine in thyroid has been determined by titration of the iodide in hydrochloric acid solution with ceric sulfate, either with ferroin as indicator or with chloroform to detect the iodine monochloride end point (*32, 61*).

Iron was one of the first materials to be titrated potentiometrically with standard ceric solution (*3, 39, 151, 152*). Early indicators used for this titration were diphenylamine after reduction of the iron with stannous chloride in hydrochloric acid solution or with aluminum or zinc in sulfuric acid solution (*136, 152*); methyl red, erio glaucine, or erio green after similar treatment of a ferric solution (*49*); and Victoria blue BX after reduction with a metal in sulfuric acid solution (*25*). Ferroin was found to be very satisfactory for this titration (*145*).

By use of a silver reductor, iron may be determined in the presence of vanadium. The latter is reduced but if the solution containing ferrous and vanadyl ions is made 5 *M* in sulfuric acid before titration, and ferroin is added as indicator, the ferrous ion alone is oxidized with ceric sulfate. Titanium, chromium, and manganese do not interfere (*147*). This method gave very accurate results for iron in ores and ferrovanadium. It was adapted to amounts of iron of the order of 10 mg. by use of 0.01 *N* ceric sulfate. With a smaller silver reductor, the method gave results for 0.68 to 2.75 mg. of iron accurate to a few thousandths of a milligram (*28*). In the microdetermination of iron, 2,2′-bipyridine has also been used as indicator (*95*).

A variation of the stannous chloride method has been proposed. After the reduction, molybdosilicic acid is added, which is reduced to molybdenum blue by the excess stannous chloride. In titrating with ceric salt the first end point occurs with oxidation of stannous chloride and the disappearance of the blue color. After adding ferroin the titration of ferrous ion is made (*139*). No application of the method was made to ores, etc.

Other variations of the microdetermination of iron have been described (*69, 115, 137*).

The oxidizing action of potassium ferrate has been checked by reduction to ferric ion with a measured excess of standard alkaline arsenite. The excess was titrated with ceric salt after acidifying with sulfuric acid and adding osmium tetroxide as catalyst and ferroin as indicator (*104*).

Magnesium has been determined by treatment of its 8-hydroxyquinolate in hot perchloric acid solution with a measured excess of standard nitratocerate, and titration of the unused cerate with ferrous sulfate, with ferroin as indicator (*94*). In the microprocedure for magnesium, standard perchloratocerate solution has been reported preferable for the oxidation (*51*).

Mercurous ion has been quantitatively oxidized to mercuric ion by a large excess of standard ceric salt acting in hot sulfuric acid solution for 30 to 60 minutes. The acidity should not be too great. The excess ceric salt was determined by potentiometric titration with standard ferrous sulfate (*161*). Mercuric ion caused no interference.

Molybdenum, after reduction with stannous chloride, titanous chloride, lead, or zinc has been titrated potentiometrically in hot solution with standard ceric sulfate. It was stated that the solution must contain a high concentration of hydrochloric acid, and some manganous sulfate to act catalytically in breaking up hydrolytic complexes of molybdenum. In some of the titrations two end points would be evident: at an oxidation state for molybdenum of +5 and of +6 (*127, 136*).

Molybdic acid may be converted to the +5 oxidation state in a 2 *M* hydrochloric acid solution at 60° to 80° C. in the silver reductor. Phosphoric acid added before the reduction causes no difficulty, and makes the subsequent titration with ceric sulfate, with ferroin as indicator, more rapid. Nitrate ion must be absent (*16*). Mercury may also serve as the reducing agent (*44*).

In the analysis of uranium-molybdenum alloys, the two elements are obtained in their hexavalent forms, after which molybdenum is precipitated in a buffered solution as thorium molybdate by the addition of thorium perchlorate. The precipitate is dissolved in hydrochloric acid and the solution passed through a Jones reductor into an excess of ferric alum containing some phosphoric acid. The solution is titrated with ceric sulfate, with ferroin as indicator (*5*).

Nitrite was employed in 1905 to titrate a solution of ceric sulfate to the disappearance of a yellow color. It was suggested that better results might be obtained from the reverse reaction: addition of an excess of ceric salt and determination of the excess (*6*). The potentiometric titration of nitrite was described in 1928 (*2, 3*). Later the titration of ceric sulfate with nitrite was found to be quantitative at 50° to 60° C. in a nitric, sulfuric, or perchloric acid medium. The tip of the buret was placed under the surface of the liquid, and the end point was determined either potentiometrically (*155, 156*) or with ferroin added within a few drops of the end point (*162*). A method for nitrite based upon the addition from a pipet of a definite volume of nitrite solution under the surface of an excess of standard ceric sulfate, and titration of latter with ferrous sulfate (*10*) has been adapted to indirect microdetermination of potassium ion after precipitation with sodium cobaltinitrite (see potassium).

Nitrogen Dioxide. In the manufacture of nitric acid it is necessary to know the amount of nitrogen dioxide in the final product. For this purpose a measured volume (an excess) of standard nitratocerate is added to a solution of dilute perchloric acid in a beaker. A sample of the nitric acid is delivered with a pipet under the surface of the cerate solution. After standing a short time, the solution is stirred, nitroferroin added, and the excess cerate titrated with sodium oxalate (*129*). The method is stated to be accurate and rapid.

Phosphorus has been precipitated as ammonium molybdiphosphate in a hydrochloric acid solution containing ammonium chloride. After filtering, the precipitate was dissolved in dilute sodium hydroxide and enough hydrochloric acid added to make the solution 2 *M* in acid. Phosphoric acid was added, the molybdic acid reduced in a silver reductor, and the pentavalent molybdenum titrated with ceric sulfate, with ferroin as indicator (*17*). Any nitrate ion in solution causes low results for molybdenum. Therefore the usual nitric acid–ammonium nitrate medium for the precipitation of ammonium molybdiphosphate has to be avoided. The method was applied to solutions containing about 6 mg. of phosphorus. The authors adapted the above procedure to the determination of phosphorus in the presence of iron (6 mg. of phosphorus to 1 gram of iron).

Plutonium sulfate solutions have been reduced to Pu(III) in a small Jones reductor, and titrated to Pu(IV) with ceric sulfate (0.0045 *N*), with ferroin as indicator. The reproducibility on 2.5 mg. of plutonium was ±0.25% (*73*).

Potassium in small amounts has been determined indirectly by precipitation with sodium cobaltinitrite, and estimation of this precipitate in various ways. It has been dissolved in excess standard ceric sulfate solution, and the excess determined either with ferrous sulfate, erio glaucine, or ferroin serving as indicator (*10, 22, 68*), or iodimetrically (*67*). Potassium has been precipitated as potassium silver cobaltinitrite. The nitrite was then liberated with hot alkali, the solution acidified and titrated with ceric sulfate, with ferroin as indicator (*71*). A comparative study has been made of permanganate and ceric sulfate for the oxidation of cobaltinitrite in the estimation of potassium in its chloride solution and in soil extracts (*55*). Both methods were found reliable. The end point with ceric sulfate, with ferroin as indicator, was sharper than the end point with permanganate.

Sodium in micro quantities may be determined indirectly by precipitation as sodium zinc uranyl acetate or sodium magnesium uranyl acetate. The precipitate is dissolved in dilute sulfuric acid, and the solution is passed through a Jones reductor. After bubbling air through the solution to oxidize any uranium(III) to uranium(IV), the latter is determined with ceric salt solution (*42*) (see uranium).

The reduction of the uranium has also been effected with saturated liquid cadmium amalgam. The solution after separation from the amalgam was aerated to oxidize uranium(III) and then titrated with ceric sulfate, with ferroin as indicator. This oxidizing solution was found to give a sharper end point than was obtained with dichromate (*62*).

Tellurium. Chromic ion has been used to catalyze the reaction between tellurous acid and an excess of standard ceric sulfate in hot sulfuric acid solution. The oxidation of the former was quantitative over a wide range of experimental conditions. Selenious acid caused no interference if the concentration of sulfuric acid at the time of oxidation was not too high. The excess ceric sulfate was titrated potentiometrically with ferrous sulfate (*160*). This procedure is reported to be more rapid and less subject to experimental conditions than the method employing dichromate in hydrochloric acid medium.

Thallium. Thallous salt may be titrated potentiometrically in hydrochloric acid solution with ceric sulfate. Considerable acid should be present for a rapid reaction at room temperature. Above 60° C. the potentiometric end point is poor. Ferric, cupric, bismuth, cadmium, lead, stannic, mercuric, zinc, selenite, tellurite, arsenate, antimonic, and chromic ions do not interfere. In the presence of chromic ion, the concentration of hydrochloric acid must be high and the temperature low to prevent oxidation (*158*). The determination may be made at 50° C. in a hydrochloric acid solution containing iodine chloride and ferroin (*162*). It has been stated that this titration may be made in the presence of iodine chloride as catalyst and chloroform as indicator (*12*), but in later work such a titration has been considered unsatisfactory (*133*).

Thiosulfate. Two methods for this ion have been found accurate. In the first, standard ceric sulfate was added by a pipet to a solution containing excess potassium iodide, and the iodine liberated was titrated with thiosulfate. If air was excluded, the results were accurate. A second method, as accurate as and more rapid than the iodometric procedure, involved the addition of a measured volume of thiosulfate solution to water containing the correct amount of potassium iodide and starch solution, followed by titration with standard ceric sulfate to the starch-iodine end point. The initial volume of solution should be sufficiently large for the acid in the ceric sulfate to cause no interference and it should be at least 10 times the volume of 0.1 *N* thiosulfate solution used. A minimum of 0.15 gram of potassium iodide is recommended per 125 ml. of initial solution (*50*).

Thorium has been precipitated from an acetic acid solution as thorium molybdate. The precipitate was dissolved in hydrochloric acid and the solution passed through a Jones reductor into an excess of ferric alum containing some phosphoric acid. The solution was titrated with ceric sulfate, with ferroin as indicator. This procedure afforded a means of separating thorium from calcium, as the latter was not precipitated as molybdate from an acetic acid solution. Although uranyl molybdate is insoluble in acetic acid solution, its precipitation was found to be delayed for several hours if ammonium acetate was present. Thus, with this modification, it was possible to separate thorium from uranium (*5*).

Tin. Early mention has been made of the potentiometric titration of stannous ion with ceric sulfate (*3*). More recently a method for tin with final titration in hydrochloric acid solution with ceric sulfate has been found quantitative. A potassium iodide–starch solution was used as indicator. Results on Bureau of Standards bearing metals in which the tin varied from 11% to more than 88% were good (*7*). Diphenylamine has been used in this same titration (*101*).

Titanium has been reduced with zinc amalgam to titanous salt, which was then titrated in an inert atmosphere with standard ceric sulfate, with diphenylamine as indicator (*136*).

Uranium. A hot solution of uranyl sulfate has been reduced with a Jones reductor and the resulting solution titrated in an inert atmosphere with ceric sulfate. Two end points were obtained ($U^{+++} \rightarrow U^{++++}$; $U^{++++} \rightarrow UO_2^{++}$), and the volume of oxidizing agent required between the two gave quantitative results for uranium. A 2% sulfuric acid medium was satisfactory for the titration. At higher concentrations of acid, results were accurate but establishment of equilibrium near the end point became slower. Results in hydrochloric acid solutions were quantitative but end points less sharp and equilibrium was reached more slowly. The reduction to trivalent uranium was small in sulfuric acid solution and a little larger in hydrochloric acid medium (*33*). A second and very similar study on reduction of uranium and subsequent potentiometric titration in steps with ceric sulfate appeared the same year. Here, reduction was made at room temperature and the authors stated that chloride interfered (*46*). Ferroin has been shown to be satisfactory in this titration in sulfuric acid solution at 50° C. (*162*).

Uranium has been quantitatively reduced in 4 *M* hydrochloric acid at 60° to 90° C. to uranium(IV), but no further, in the silver reductor. Titration of uranous salt at 50° C. with ceric sulfate, with ferroin as indicator, was considered unsatisfactory, but the same titration was found to be rapid and the end point sharp, if made at room temperature in the presence of a little phosphoric acid. Acetic acid did not interfere. Those materials reduced in the silver reductor (iron, molybdenum, vanadium, copper) must be absent (*15*).

Reduction of uranium to the quadrivalent state with a zinc spiral in a solution containing hydrochloric and perchloric acid, followed by titration with ceric salt, with ferroin as indicator, has been described (*84*).

Vanadium. The potentiometric titration of vanadyl ion with ceric sulfate has been shown to be quantitative at 70° to 75° C. in sulfuric, hydrochloric, or perchloric acid solution, with a more rapid reaction at the end point in the latter two acid media. In a sulfuric acid medium at 70° to 75° C. vanadyl ion was oxidized selectively in the presence of chromic ion. Ferric and manganous salts caused no interference. Considerable tungstic acid, held in solution by ferric salt, could also be present during this potentiometric titration. The method was adapted to the analysis of chrome-vanadium and chrome-vanadium-tungsten steels for vanadium (*150*).

A somewhat lower temperature (50° to 60° C.) has been recommended for this same titration. The method was applied to the analysis of ferrovanadium (*40*).

The differential potentiometric titration of ferrous and vanadyl perchlorates in 8 *N* perchloric acid has been described. Excellent end points were obtained. The oxidizing agent was nitratocerate in perchloric acid solution. With the vanadyl-vanadate electrode potential considerably higher than its normal value in this

very acidic medium, an oxidizing agent stronger than sulfatocerate or permanganate solution would be required (*117*).

Zinc. An indirect method based on addition of a measured excess of standard potassium ferrocyanide to a sulfuric acid solution containing zinc ion has been studied. After the solution has stood for 15 minutes the excess ferrocyanide was titrated potentiometrically with ceric sulfate (*130*). A slight variation in this method, applied to the determination of zinc in magnesium alloys, made use of ferroin in the final titration (*91*).

Organic Compounds. Uses of cerate salts in determining organic compounds are multiplying rapidly. A strong oxidizing solution which can be heated with organic materials for a period of time without undergoing decomposition itself, and the excess of which can be determined simply, is very desirable. Some applications in this field follow.

ORGANIC ACIDS. In the reaction between tartaric acid and excess ceric sulfate, formic acid, one of the oxidation products, was found to be completely stable (*11*). Permanganate, in contrast, acts slowly on formic acid. Different opinions were expressed in this early work on the course of the reaction between tartaric acid and ceric sulfate (*11, 12*). The action of an excess of this oxidizing agent on a number of organic acids in hot sulfuric acid solution over periods ranging from 15 to 120 minutes was determined by potentiometric titration of excess ceric sulfate with ferrous sulfate. Of the acids studied, tartaric, malonic, malic, glycolic, and citric acid were oxidized extensively and to a definite degree. Carbon dioxide and formic acid were ordinarily formed. The variation in conditions over which identical results were obtained made possible the use of a factor in calculating results. In these same experiments formic, acetic, succinic, fumaric, and maleic acids were found not to be oxidized, and benzoic, phthalic, and salicylic acids to be oxidized to a variable degree (*159*). A similar procedure has been followed in determining pyruvic acid, a mole of which was oxidized to acetic acid and carbon dioxide by two equivalents of ceric ion (*37*). A mole of L-ascorbic acid has been reported to require six equivalents of ceric ion for oxidation (*131*).

REDUCING SUGARS AND STARCHES. Many have used a cerate solution in the determination of reducing sugars. The sugar was treated with an excess of Fehling's solution (*14, 126*) or of ferricyanide in alkaline medium (*9, 31, 56, 57, 143, 144, 148*), and the cuprous oxide or ferrocyanide formed has been estimated by the usual procedures employing ceric salts.

The ferricyanide method has been used to obtain the reducing power of starches and dextrins (*34, 58*).

HYDROQUINONE has been titrated in acid solution at room temperature with ceric salt. The end point was determined potentiometrically, with diphenylamine, or less satisfactorily with methyl red added near the end of the titration. Either a sulfuric or hydrochloric acid medium was satisfactory (*48*). A later study of the iodometric and cerimetric methods in the assay of hydroquinone showed the latter method to be more accurate. Ferroin was recommended as indicator (*76*).

GLYCEROL has been oxidized in acid solution with a measured excess of standard ceric sulfate by allowing the mixture to boil under a reflux condenser for an hour. The solution was cooled and the excess ceric salt determined with ferrous sulfate, with xylene–cyanol FF as indicator. One mole of glycerol required 8 equivalents of ceric ion for oxidation (*26*). A method for glycerol, in the presence of dextrose, applicable to a fermented medium has been described (*38*). A more rapid procedure for glycerol is based on its oxidation in perchloric acid solution with a measured excess of standard perchloratocerate solution at 50° C. Only 15 minutes are necessary for the oxidation. After cooling, the excess cerate is titrated with sodium oxalate, with nitroferroin as indicator (*111*).

OTHER ORGANIC COMPOUNDS. Further experiments using excess perchloratocerate ion in oxidizing organic substances in perchloric acid solution have been carried out and the results obtained compared with those obtained from using periodate in excess (*112*). These authors state the general principles governing such oxidations (*106*, pp. 88–123) and give the usual procedure followed. Where this method may be used, results are stoichiometric—that is, a definite number of equivalents of cerate are used per mole of organic substance. The methods are not specific in their action but require preliminary separation of the substance being determined from any interfering substances. In a recent article (*53*), results from the use of ceric salts, usually ceric sulfate, in determining organic compounds agree substantially with determinations described above.

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Ultraviolet Spectrophotometric Determination of Columbium

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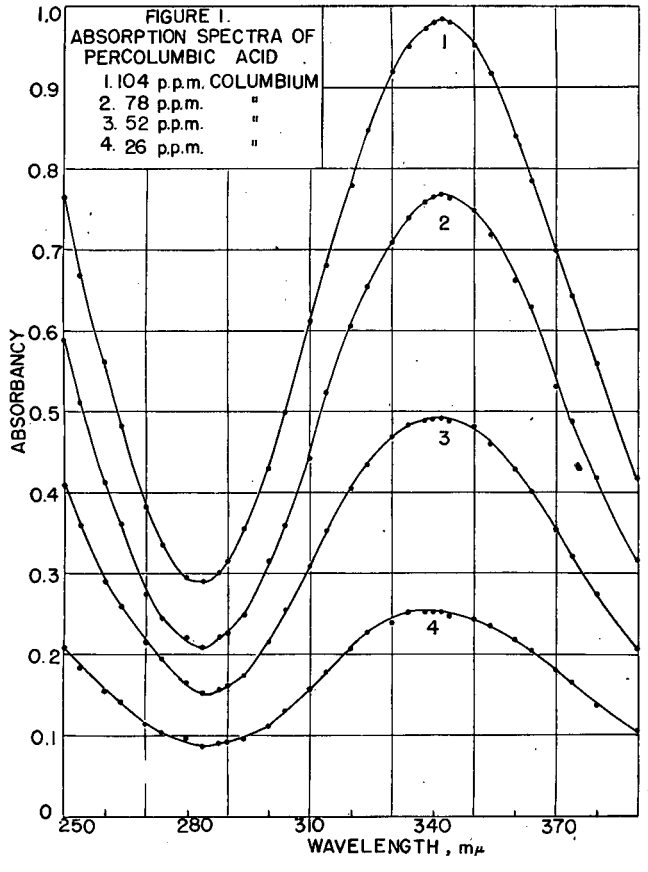
An investigation was undertaken of conditions under which columbium can be determined spectrophotometrically as percolumbic acid. Formation of the percolumbic acid complex in a concentrated acidic mixture of sulfuric and phosphoric acids results in a stable yellow hue exhibiting maximum absorbancy in the ultraviolet region. The system conforms to Beer's law at 342 mμ. The optimum concentration using 1-cm. cells is from 0 to 125 p.p.m. of columbium. The effects of acid concentration, hydrogen peroxide concentration, and diverse ions were determined. The main interferences are due to ferric, molybdate, vanadate, titanic, tungstate, nitrate, chloride, and fluoride ions. The method is simple, rapid, and accurate. The ultraviolet spectrophotometric method for the determination of small amounts of columbium shows a marked increase in sensitivity over the colorimetric method.

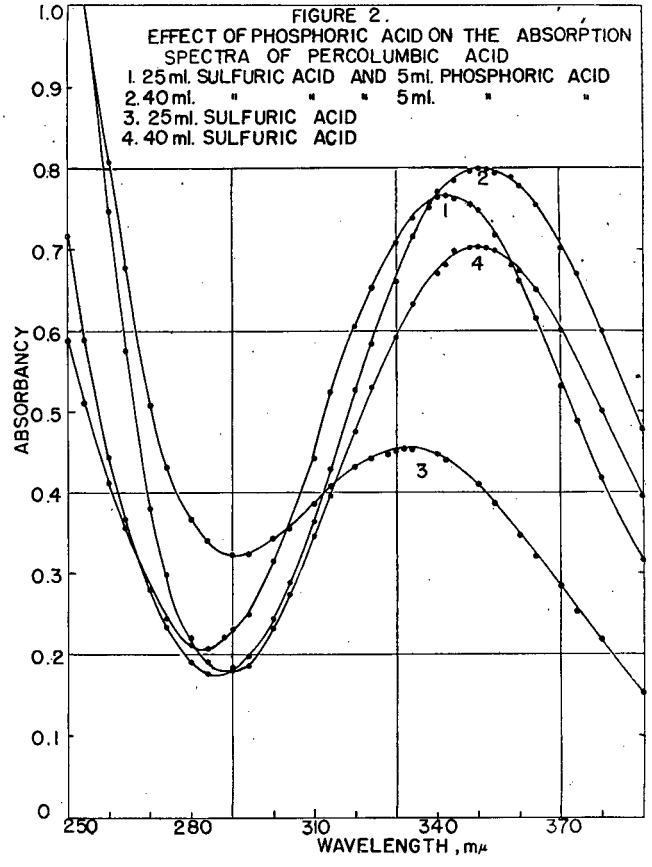
IN AN investigation of the ultraviolet absorption spectra of per acids and peroxy complexes the authors have shown that characteristic absorbancy maximums in the ultraviolet region are suitable for the determination of small amounts of molybdenum (*5*) and vanadium (*6*). This paper presents the characteristic ultraviolet absorption spectrum of percolumbic acid, which is the basis of a more sensitive spectrophotometric method of determining columbium.

Columbium has been determined colorimetrically by utilizing the faintly yellow color resulting from the treatment of a moderately concentrated sulfuric acid solution of a columbate with hydrogen peroxide (*2–4*). Thanheiser (*7*) used a sulfuric-phosphoric acid solution to minimize the interference due to titanium. Geld and Carroll (*1*) determined columbium in high temperature alloys colorimetrically as percolumbic acid. They removed molybdenum and made corrections for the tungsten and titanium present. As a survey of the literature showed no spectrophotometric data on percolumbic acid, it seemed advisable to investigate the absorption spectra of this per acid.



APPARATUS AND SOLUTIONS

The absorbancy measurements were made with a Beckman Model DU spectrophotometer and 1.000-cm. silica cells. The spectrophotometer was equipped with an ultraviolet-sensitive phototube for high sensitivity in the 220 to 625 mμ region of the spectrum.



A standard columbium solution was prepared by fusing 1.00 gram of columbium pentoxide with 10 grams of potassium pyrosulfate in a platinum crucible. The melt was cooled, dissolved in 100 to 150 ml. of a saturated ammonium oxalate solution, and diluted to 500 ml. This solution was standardized gravimetrically according to the following procedure. A 25-ml. aliquot was

treated with 10 ml. of 72% perchloric acid and the solution evaporated until copious white fumes of perchloric acid were given off and a white curdy precipitate of columbic acid settled out. The hot solution was filtered and the precipitate washed thoroughly with hot 1 to 20 hydrochloric acid. The precipitate was ignited and weighed as Cb_2O_5. One milliliter of this solution contained 1.30 mg. of columbium. It is necessary to filter the solution at elevated temperature in order to take advantage of the high solubility of potassium perchlorate under these conditions and thereby eliminate the danger of contaminating the columbic oxide precipitate with potassium perchlorate.

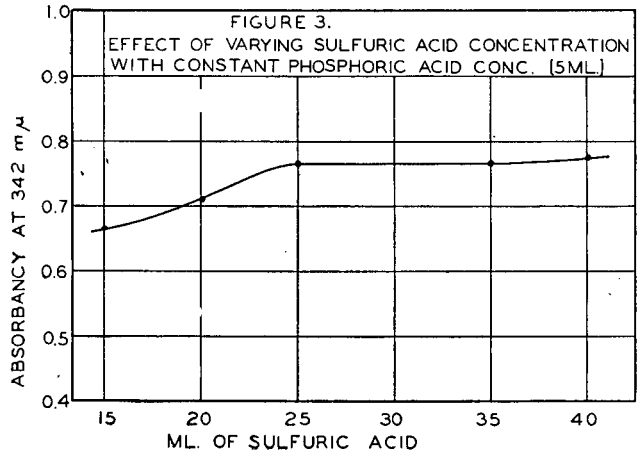
The standard columbium solution was examined spectrographically using the rotating electrode technique. Traces of molybdenum, titanium, and tantalum were found.

The hydrogen peroxide used was 3% analytical reagent grade. The sulfuric acid was 96% reagent grade and the phosphoric acid was 85% reagent grade.

FUNDAMENTAL REACTION

Treatment of a concentrated sulfuric acid solution of columbium with hydrogen peroxide results in the formation of percolumbic acid. This acid has a characteristic yellow color with an absorbancy maximum in the ultraviolet region.

In order to study the effect of certain variables on the maximum absorbancy, the following general procedure was used.



A definite amount of the standard columbium solution was added by means of a microburet to a 50-ml. volumetric flask. The desired amount of sulfuric and phosphoric acids was added and the volume was adjusted to 50 ml. with redistilled water. The solution was allowed to cool to room temperature. After the addition of 1 ml. of 3% hydrogen peroxide, the solution was thoroughly mixed. Absorbancy measurements were taken from 250 to 500 mμ at 2 mμ intervals. The system is stable for at least 24 hours. In the study of diverse ions, a definite amount of the solution containing each ion was added before dilution and addition of the hydrogen peroxide.

EFFECT OF VARIABLES

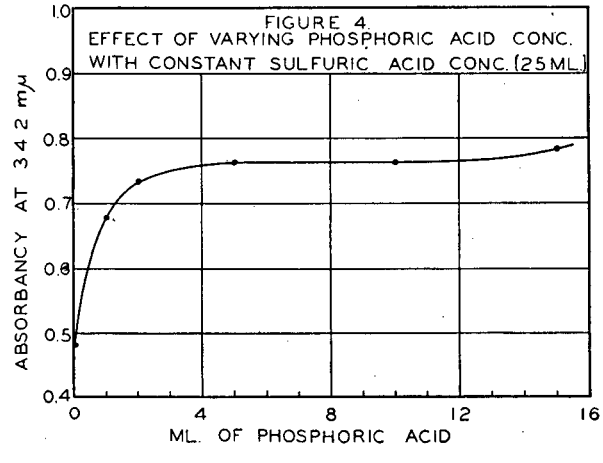
Columbium Concentration. The absorption spectra for various concentrations of columbium were determined and conformity to Beer's law was found at 342 mμ, in concentrations from 0 to 125 p.p.m. of columbium. When a sulfuric-phosphoric acid solution was used, a good absorbancy maximum occurred at 342 mμ, as shown in Figure 1. There is no absorbancy maximum in the visible region.

Acid Concentration. The effect of various concentrations of sulfuric acid was determined using 78 p.p.m. of columbium. It was found that 25 ml. of concentrated sulfuric acid produced a color with an absorbancy maximum at about 330 mμ. However, the Beer's law line did not go through the origin when a reagent blank was used as a reference. When an unperoxidized columbium solution was used as a reference, the absorbancy maximum at 330 mμ was obtained, but the shape of the curve was different in the 250 to 300 mμ region where it was determined that the columbic acid has an appreciable absorbancy. The use of the unperoxidized solution in the reference cell also failed to bring the Beer's law plot through the origin. This behavior indicated the possibility of incomplete formation of percolumbic acid. When 40 ml. of concentrated sulfuric acid were used there was a shift in the absorbancy maximum to about 350 mμ with a large increase in absorbancy (Figure 2).

Table I. Interfering Diverse Ions

Ion	Added as	Added, P.P.M.	% Error	Permissible Amount, P.P.M.
Fe^{+++}	$Fe(ClO_4)_3$	100	+61.0	0
VO_3^-	NH_4VO_3	111	+4.0	25
MoO_4^{--}	Na_2MoO_4	13	+1.3	15
Ti^{++++}	$Ti(SO_4)_2$	10	+4.6	5
NO_3^-	$NaNO_3$	500	+23.0	100
F^-	NaF	24	−2.1	10
SCN^-	NaSCN	1000	+21.4	100
Cl^-	NaCl	500	+11.1	100
Br^-	NaBr	1000	+12.6	100
BrO_3^-	$NaBrO_3$	1000	+9.3	100
NO_2^-	$NaNO_2$	500	−58.6	0
GeO_3^{--}	Na_2GeO_4	50	+6.0	15
ClO_3^-	$NaClO_3$	100	+100.0	0
Cr^{+++}	$CrCl_3$	500	+6.2	200
$Cr_2O_7^{--}$	$K_2Cr_2O_7$	575	−12.3	100
UO_2^{++}	$UO_2(C_2H_3O_2)_2$	1000	+5.9	500
WO_4^{--}	Na_2WO_4	140	+13.4	10
Be^{++}	$BeSO_4$	1000	+23.8	50

Thanheiser (7) stated that phosphoric acid seemed to enhance the color of the complex and increase its stability. Consequently, sulfuric-phosphoric acid mixtures were tried. It was found that 5 ml. of 85% phosphoric acid with 25 ml. of sulfuric acid in a volume of 50 ml. gave an absorbancy maximum at 342 mμ, as shown in Figure 2, with an absorbancy larger than that obtained with 40 ml. of sulfuric acid. The use of 40 ml. of sulfuric acid and 5 ml. of phosphoric resulted in a shift of the absorbancy maximum to about 350 mμ and a slight increase in absorbancy. From a practical viewpoint the use of 25 ml. of sulfuric acid and 5 ml. of phosphoric acid per 50 ml. was deemed most suitable. That 25 ml. of sulfuric acid is the minimum amount of sulfuric acid to be used with 5 ml. of phosphoric acid is shown in Figure 3, and that 5 ml. of phosphoric acid is the optimum amount to be used with 25 ml. of sulfuric acid is shown in Figure 4.



Hydrogen Peroxide Concentration. The effect of various concentrations of hydrogen peroxide was studied using 78 p.p.m. of columbium and 25 ml. of sulfuric and 5 ml. of phosphoric acid in a final volume of 50 ml. It was found that 1 ml. of 3% hydrogen peroxide resulted in the attainment of maximum absorbancy and that up to 7 ml. the absorbancy remained constant. Therefore, for

convenience in transfer with a 1-ml. pipet, 1 ml. of 3% hydrogen peroxide is sufficient for attainment of maximum absorbancy as measured at 342 mμ.

Effect of Diverse Ions. The effect of the diverse ions was studied using 78 p.p.m. of columbium with an acidic mixture of 25 ml. of sulfuric and 5 ml. of phosphoric acid. The absorbancy measurements were taken at 342 mμ in order to ascertain any deleterious effects of the various ions. A negligible error has been obtained with 1000 p.p.m. of aluminum, acetate, arsenate, cadmium, cerium, cobaltous, cupric, citrate, calcium, bismuth, carbonate magnesium, manganous mercuric, malonate, nickelous, oxalate, perchlorate, stannate, tartrate, tetraborate, thiosulfate, silver, lithium, iodate, and zinc ions. It was found that 150 p.p.m. of tantalum did not interfere. The following ions interfere because of the formation of precipitates due either to the acids present or to columbate ions: barium, plumbous, strontium, zirconyl, ferrocyanide, silicate, and iodide. Table I lists the interfering ions and their effect.

SUMMARY

A high concentration of sulfuric acid and the addition of phosphoric acid are important for the development of percolumbic acid exhibiting maximum absorbancy in the ultraviolet region. The effect of 51 diversions was determined. Ferric, molybdate, titanic, chlorate, chloride, nitrate, nitrite, fluoride, vanadate, and tungstate ions are the chief sources of error. The ultraviolet spectrophotometric method that was developed is more sensitive than the conventional colorimetric method for determining columbium as percolumbic acid.

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Spectrophotometric Determination of Rhodium with Hypochlorite

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This study was undertaken to investigate the possible application, for spectrophotometric determination of rhodium, of the blue color formed by treatment of rhodium(III) with sodium hypochlorite. Below pH 3.5, very little color developed; above pH 10, a dark blue-green precipitate formed. Within the pH range 4.7 to 7.2, maximum constant blue color was produced. At room temperature about 1 hour was required for maximum color development; the resulting color was stable for an hour, after which slow fading occurred. The color could be restored by addition of more hypochlorite. Heating accelerated both the developing rate and the fading rate. The system has a transmittancy minimum at 665 mμ, and conforms to Beer's law. Palladium, platinum, gold, iron, chromium, and nickel ions can be tolerated in relatively large amounts, and ruthenium, osmium, iridium, cobalt, manganese, and copper in moderate quantities relative to rhodium. Salts of iridium and cobalt catalyze the decomposition of the hypochlorite. Of the common anions, only iodide and iodate interfere. When transmittancy measurements are made at 665 mμ in 1-cm. cells, the optimum range is about 5 to 20 p.p.m. of rhodium; in this range maximum photometric accuracy corresponds to about 0.6% relative error.

THE determination of rhodium by precipitation either as hydrous oxide or as sulfide, followed by ignition in hydrogen or by reduction of its compounds with active metals or with titanium(III) salts (*6*, p. 274 *et seq.*; *8*) is tedious and subject to many possible sources of error. Rhodium has been determined gravimetrically with thiobarbituric acid (*4*). Many organic nitrogen compounds form colored precipitates with rhodium(III), some of which have been used for microscopic identification (*10*). The red color produced by treating rhodium(III) with tin(II) chloride in hydrochloric acid solution (*7*) has been used as a test for rhodium (*9*, *11*), and also for its estimation (*3*).

Demarçay (*5*) reported that rhodium solutions treated with sodium hypochlorite gave a yellow precipitate, soluble in acetic acid, and that the solution slowly changed to orange yellow, followed by the formation of a gray precipitate and a sky-blue solution. Alvarez (*1*) observed that when chlorine was passed into a solution of a rhodium salt in sodium hydroxide the liquid became yellowish-red, then deep red, followed by formation of a green precipitate, which finally dissolved forming a blue solution. It was the purpose of the present investigation to study the formation of the blue reaction product with a view to its application as a spectrophotometric method for the determination of rhodium.

REAGENTS

Rhodium metal powder was obtained from A. D. Mackay, Inc. Spectrographic examination of the sample detected no osmium nor ruthenium, and only trace quantities of palladium, platinum, iridium, gold, copper, and silver (amounts far below the tolerance limits in the determination of rhodium with hypochlorite). Sodium hypochlorite was used in the form of Chlorox bleaching solution. All other chemicals were analytical reagent grade.

APPARATUS

A Beckman Model DU spectrophotometer, operated at high constant sensitivity, was used for the transmittancy measurements. The slit width for measurements at 665 mμ was 0.08 mm. The matched Corex cells had a 1.000-cm. light path.

EXPERIMENTAL

Preparation of Standard Sample. Weighed samples of rhodium metal powder were placed in a small porcelain boat and mixed with finely ground and previously ignited sodium chloride; 1

gram of sodium chloride was used for each 0.1 gram of rhodium. The mixture was heated in a combustion furnace at 750° C., while chlorine was passed through the combustion tube at a rate of about 500 ml. per minute. Although conversion was not quantitative in 5 hours (*6*, p. 274), by the end of 2 hours about 98% of the rhodium was converted to the soluble chloro-compound. The melt was dissolved in water containing 5 ml. of hydrochloric acid in 250 ml., and insoluble material filtered off. After the filter paper was burned off, the residue was again treated with sodium chloride and chlorine. By this procedure the conversion of the rhodium was complete. The combined solutions, which were a light raspberry-red color, were diluted to known volume.

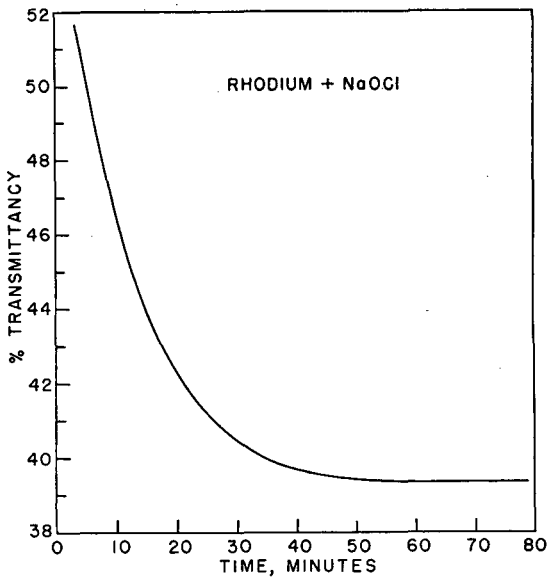

Figure 1. Development of Color

Development of Color. When treated with sodium hypochlorite, solutions of rhodium(III) chloride developed a blue color, provided the pH of the solution was neither too low nor too high. The color is very similar to that of ammoniacal solutions of copper(II) and to solutions of cobalt(II) chloride in ethyl alcohol or in concentrated hydrochloric acid. At room temperature (about 25° C.) the color developed slowly and reached maximum intensity in about 50 minutes (see Figure 1). The color was then stable for at least an hour, after which it began to fade slowly. When the reaction mixture was heated, the color intensity increased more rapidly for a short time, but the rate of fading was accelerated. Solutions that had faded by aging could be restored to full color intensity, for the amount of rhodium represented, by the addition of more hypochlorite.

Based upon the above facts, and upon the results of a study of the effects of pH (see below), the following standardized procedure was adopted: Ten milliliters of acetate buffer solution (50 ml. of glacial acetic acid and 200 grams of sodium acetate per liter) were mixed with 50 ml. of 5% sodium hypochlorite solution. An appropriate aliquot of the stock standard solution, to give the final concentration of rhodium desired, was added to the mixture and the solution was made up to 100 ml. After standing at room temperature for 1 hour, the transmittancy was measured, using as a blank a similar solution of reagents. If the rhodium solution was mixed with the acetate buffer and allowed to stand for some time before the addition of hypochlorite, the color was less intense than when the hypochlorite was added immediately; the difference in color intensity was roughly proportional to the time elapsed before the addition of the hypochlorite. When the reactants were mixed in rapid succession, good reproducibility of color was attained, regardless of the order of addition of reactants. The transmittancy of replicate samples was consistently reproducible to 0.2% (absolute).

Spectral curves for several rhodium concentrations are shown in Figure 2, which covers the wave-length range from 800 to 400 mμ. Below 400 mμ the transmittancy continues to decrease slightly, reaching a minimum at about 375 mμ, after which it increases rapidly to about 100% at about 340 mμ. The transmittancy minimum at 665 mμ was used for subsequent measurements. The color system conforms to Beer's law over the concentration range investigated (up to 40 p.p.m.).

Effect of Reagent Concentration. When varying amounts of hypochlorite reagent were used with fixed amounts of rhodium and buffer, the transmittancy decreased rapidly with increasing amounts of hypochlorite, up to about 40 ml. of hypochlorite solution per 100 ml. of final solution; the transmittancy was then constant with increasing amounts of hypochlorite (Figure 3). To provide a safe margin for routine work, 50 ml. of hypochlorite were used in the procedure finally adopted.

Effect of pH. It was apparent from the outset that the pH of the final solution had a marked effect on the color development. In order to establish optimum conditions of pH, samples of the acidic rhodium(III) solution were treated with varying small amounts of dilute sodium hydroxide and the color was developed with hypochlorite. The pH of the final solution was measured with a Beckman pH meter. Figure 4 shows the relation between transmittancy and the pH of the solution, for a constant amount of rhodium (8 p.p.m. in the final solution). Constant minimum transmittancy was obtained when the pH of the solution was within the limits of 4.7 to 7.2.

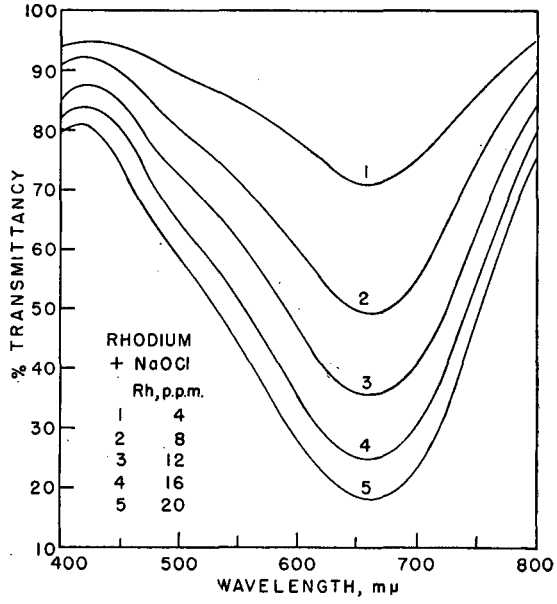

Figure 2. Spectral Curves for Rhodium

Because the rhodium(III) chloride stock solution contained hydrochloric acid, and the hypochlorite solution was alkaline, the use of a buffer was indicated, to ensure in each sample a constant pH within the above range. Citrate, benzoate, phosphate, and acetate buffers were tried; only the phosphate and the acetate buffers were suitable. Citrate buffers accentuated the fading of the color; benzoate buffers lacked the capacity and range desired. The use of the acetate buffers was adopted for the standardized procedure described above. In the series measurements for constructing the standard curve, the final solutions had a pH of 6.2.

Effect of Diverse Ions. In order to form a preliminary estimate of possible interference by various ions, especially the ions of the other platinum metals, observations were made on solutions of various ions treated with acetate buffer and hypochlorite reagent. Varying amounts of the ion under investigation were then added to a constant amount of rhodium, the color was developed by the standardized procedure, and the transmittancy was measured at 665 mμ. The tolerance of the rhodium system for the contaminating ion was taken as the amount of that substance

Table I. Effect of Diverse Ions

(All solutions contained 8 p.p.m. of rhodium)

Interfering Substance	Visual Color, Interfering Substance + Reagents	Visual Color,[a] Rh + Interfering Substance + Reagents	Amount Tolerated, P.P.M.
Palladium(II)	Red	Red-amber	200
Platinum(IV)	Yellow[b]	Green	50
Ruthenium(III)	Red-yellow[b]	Blue	10
Osmium(IV)	Black colloid	Blue-black, opaque	6
Iridium(IV)	Yellow then violet	Blue	3
Gold(III)	Yellow[b]	Blue-green	15
Iron(III)	Red-brown ppt.	Blue[c]	70[c]
Cobalt(II)	Olive-green	Blue	5
Nickel(II)	Black ppt.	Blue[c]	20[c]
Manganese(II)	Black ppt.	Blue[c]	5[c]
Chromium(III) or (VI)	Yellow	Green	15
Copper(II)	Blue-green	Blue	5
Iodide, Iodate	Colorless	Blue	1

[a] Color at tolerance concentration of interfering substance.
[b] Same color as solution of test ion.
[c] Observations made after filtration.

which gave a transmittancy not more than 0.4% (absolute) different from that of the rhodium alone. The results of the interference tests are shown in Table I. Chloride, bromide, bromate, perchlorate, nitrate, sulfate, and phosphate gave no interference up to at least 100 p.p.m.; hence higher concentrations were not tried.

The visual color of the developed solutions containing rhodium and a contaminating ion were, in some cases, markedly different from the color when rhodium alone was present, without influencing appreciably the transmittancy at 665 mμ. For example, a solution containing 8 p.p.m. of rhodium and relatively large amounts of palladium was a dark red-amber color, but the transmittancy at 665 mμ was very little influenced by the palladium. In the cases of iridium and of cobalt compounds, either alone or in the presence of rhodium, catalytic decomposition of the hypochlorite to form oxygen was very pronounced. This catalytic action is being investigated further.

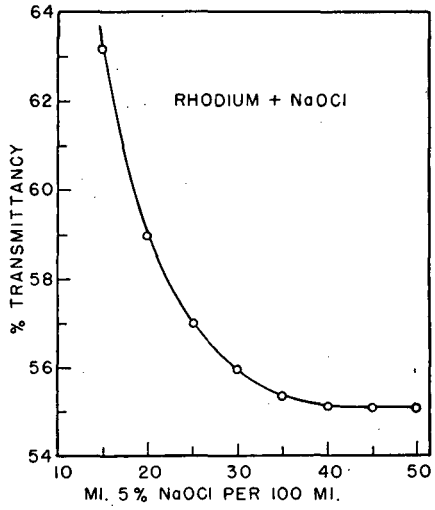

Figure 3. Effect of Reagent Concentration

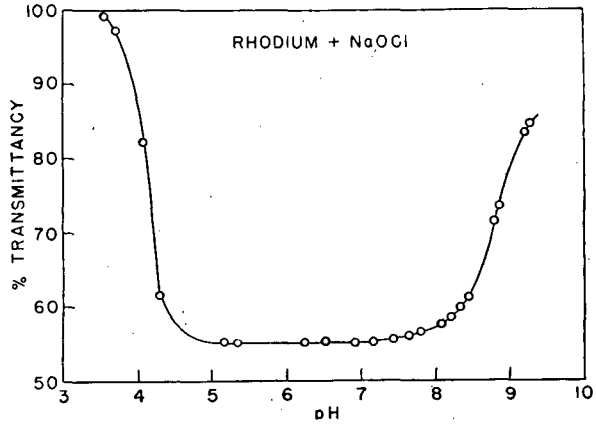

Figure 4. Effect of pH

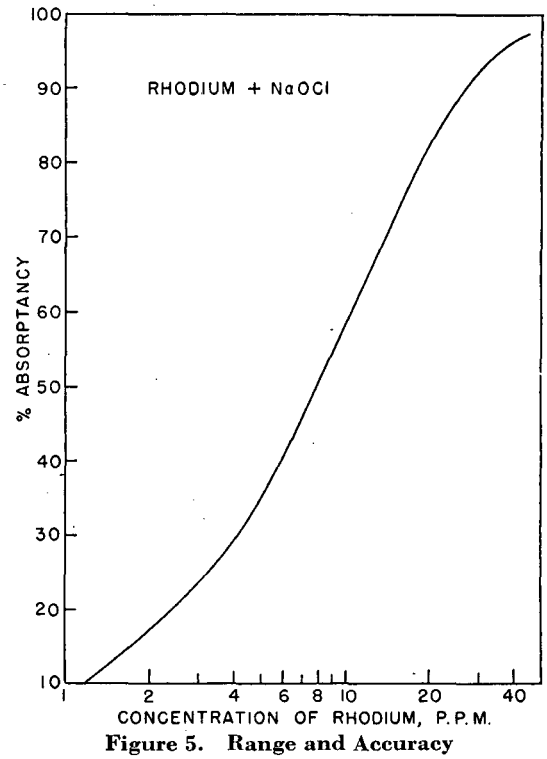

Figure 5. Range and Accuracy

Range and Accuracy. In Figure 5, standard series data are plotted as per cent absorptancy (100 − % transmittancy) against logarithm of concentration (*2*). The concentration range for best accuracy, for the conditions and technique used, is about 5 to 20 p.p.m.; in this range the relative analysis error is 2.8% per 1% absolute error in transmittancy. For a precision of 0.2% absolute transmittancy, the relative error is therefore about 0.6% in the concentration range given above. Relative errors of photometric origin will not exceed 1% in the concentration range 3 to 25 p.p.m.

DISCUSSION

At no time during this investigation did the authors observe the series of color changes recorded by Demarçay (*5*), to which reference was made above. By the procedure described the change was always from the pale raspberry-red color of the rhodium(III) chloride solution to an immediate, although faint, blue color, which increased in intensity as the mixture was allowed to stand, finally giving a deep blue solution. A yellow to red solution was not observed; in samples at a pH greater than 10, a blue or blue-green precipitate formed.

When chlorine gas was passed into alkaline solutions of rhodium(III), many of the changes of color and of state reported by Alvarez (*1*) were confirmed, although the final mixture was purple and turbid, rather than a clear blue solution. It appears likely that many of the observed changes are dependent upon the pH changes accompanying the reaction of chlorine with the alkali present.

In the analytical method described herein, the production of

Table II. Spectral Characteristics of Rhodium-Hypochlorite Solutions at Various pH Values

pH	Visual Color	Transmittancy Minimum, mμ	Transmittancy Maximum, mμ
2	Lavender	565	460
6	Blue	665	480
8	Green	665	480
10	Yellow-orange	435	385, 640

maximum blue color, within the appropriate pH range, required an extremely high ratio of hypochlorite to rhodium. For a study of the system to deduce the composition of the complex by the method of continuous variation or by the method of mole ratios, the concentration of rhodium was increased and the concentration of hypochlorite was decreased to bring the ratio of reactants into a range suitable to these methods. It was then observed that for a given ratio of hypochlorite to rhodium, various colors appeared as the pH of the solution was varied. Starting with the acidic solution of rhodium and hypochlorite (in amounts to give a final solution 0.001 *M* in each reactant), slow addition of sodium hydroxide to increase the pH caused the appearance of different colors, as listed in Table II. The color changes were completely reversible upon decreasing the pH by slow addition of dilute hydrochloric acid.

The production of a green color at a pH intermediate between that at which the blue and the yellow-orange color appeared suggested that the visual green color might be a composite of a blue- and a yellow-colored species. The spectral curves for the different solutions had transmittancy minima and maxima shown in Table II. The absorption of the yellow-orange solution at 435 mμ is sharp and intense, but the spectral curve for the green solution shows no indication of increased absorption at this wave length. The yellow-orange variety appears to be a colloidal material. All the color systems are being investigated further.

ACKNOWLEDGMENT

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Spectrophotometric Studies on Raw Cane Sugars in Solution

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In a previous study of the color of refined sugars in solution it was found that the absorbancy index determined at 560 mμ, but not at other wave lengths, is equivalent to the color expressed in terms of brightness, purity, and dominant wave length. This work has been extended to 102 raw cane sugars from eleven countries. The transmittancy of 60 Brix solutions, filtered through Celite analytical filter aid, was measured throughout the visible spectrum. The plotted transmittancy curves were smooth, and similar to those of the refined sugars. The brightness, purity, and dominant wave length were computed from the transmittancies of the solutions, and a statistical analysis showed a correlation coefficient of 0.9992 between those three and the transmittancy determined under the same conditions at 560 mμ. Consequently, the corresponding absorbancy index at that wave length gives a measure of the color of the sugar within the limit of error of transmittancy measurements. Absorbancy indexes at any other wave length give erroneous color values. It is concluded that the color of raw cane sugars can be determined in the same manner as refined sugars, confirming the statement of Peters and Phelps.

A PREVIOUS study (*5*) on the color of 76 refined sugars in solution proved the correctness of the findings of Peters and Phelps (*4*) that the absorbancy index at wave length 560 mμ is equivalent, colorimetrically, to the integral absorption over the visible spectrum. In the present work the color of the sugar solution, as perceived by the eye, was computed in terms of the monochromatic analysis—i.e., brightness (luminance), excitation purity, and dominant wave length—by the selected ordinate method of Hardy (*2*) for illuminant C of the International Commission on Illumination, and the color thus expressed was compared statistically with the absorbancy index, *a*, at wave length 560 mμ, and with the transmittancy for the same wave length at 60 Brix and a thickness of 5 cm. It was shown that the absorbancy index of refined sugars at wave length 560 mμ is equivalent to the color within the limit of error of transmittancy measurements.

This study has been extended to 102 raw cane sugars, including 40 from Cuba, 10 each from Puerto Rico, Hawaii, the Philippines, and British West Indies, 8 from Louisiana, 5 from Peru, 4 from Australia, 2 each from the Dominican Republic and Florida, and 1 from Mauritius.

Solutions of approximately 60 Brix were prepared and filtered with Celite analytical filter aid, instead of with asbestos, for reasons explained in the previous paper. The transmittancies of the filtered solutions were measured with a Coleman Universal spectrophotometer at 13 points from 405 to 700 mμ, in cells of 2.46-

Table I. Filtered Solutions in Order of Increasing Absorbancy Index

No.	Brightness	Purity	Domin. Wave Length	a, 560 Mμ	a, 420 Mμ	T, 560 mμ, 60 Brix, 2.46 Mm. Found	T, 560 mμ, 60 Brix, 2.46 Mm. Calcd.	Q, 420 mμ / 560 mμ
18	94.37	4.91	575.4	0.232	0.899	90.4	89.8	3.88
22	93.10	6.90	573.7	0.278	1.284	88.5	87.9	4.62
43	93.08	6.45	573.7	0.291	1.244	88.1	87.8	4.27
41	93.20	6.68	573.3	0.292	1.261	88.0	88.0	4.32
23	92.34	7.74	573.6	0.311	1.385	87.3	86.7	4.45
21	92.06	8.24	574.3	0.329	1.481	86.6	86.4	4.50
25	89.81	11.22	573.9	0.413	2.076	83.5	83.0	5.03
64	89.55	11.84	573.7	0.430	2.161	82.9	82.6	5.03
26	89.47	12.10	577.2	0.434	2.076	82.7	82.8	4.78
27	89.65	9.80	573.8	0.434	1.844	82.7	82.5	4.25
42	89.44	10.15	574.3	0.443	1.891	82.4	82.2	4.27
14	88.57	14.98	574.0	0.452	2.549	82.1	81.5	5.64
70	89.06	14.87	573.7	0.458	2.733	81.9	82.3	5.97
6	88.87	12.56	574.9	0.459	2.161	81.8	81.7	4.71
24	88.53	13.50	574.3	0.472	2.336	81.4	81.2	4.95
73	88.47	13.34	573.9	0.477	2.495	81.2	81.1	5.23
33	88.57	10.31	574.0	0.480	2.007	81.1	80.7	4.18
72	88.21	14.87	573.8	0.487	2.676	80.8	80.9	5.50
17	87.90	12.75	574.6	0.506	2.270	80.2	80.0	4.49
12	87.68	14.68	574.4	0.516	2.534	79.8	80.0	4.91
51	87.19	15.41	573.9	0.531	2.848	79.3	79.2	5.36
28	87.44	12.56	574.4	0.536	2.336	79.1	79.2	4.36
62	87.09	15.81	574.7	0.536	2.823	79.1	79.2	5.27
93	87.24	14.63	574.0	0.543	2.708	78.9	79.2	4.99
88	86.99	13.13	574.1	0.545	2.457	78.8	78.5	4.51
40	86.90	13.88	574.8	0.550	2.464	78.6	78.5	4.48
50	86.83	11.22	574.3	0.574	2.175	77.8	77.9	3.79
44	86.37	11.76	573.8	0.580	2.292	77.6	77.2	3.95
16	86.06	15.51	575.1	0.600	2.774	76.9	77.4	4.62
82	85.29	18.60	574.9	0.619	3.279	76.3	76.6	5.30
86	85.31	16.56	574.6	0.625	3.028	76.1	76.2	4.85
60	85.23	17.23	575.0	0.630	2.993	75.9	76.2	4.75
94	85.02	18.68	574.9	0.630	3.279	75.9	76.1	5.21
78	84.90	17.56	574.7	0.637	3.279	75.7	75.7	5.15
63	84.72	18.60	574.6	0.641	3.288	75.6	75.6	5.13
29	84.74	18.14	575.1	0.646	3.063	75.4	75.6	4.74
98	83.91	21.20	575.4	0.654	3.645	75.1	74.7	5.57
59	84.47	17.72	575.3	0.659	3.170	75.0	75.0	4.81
4	84.43	15.84	575.2	0.670	2.857	74.6	74.7	4.26
52	84.42	16.88	575.0	0.673	3.036	74.5	74.8	4.51
61	84.18	19.03	574.9	0.675	3.420	74.4	74.7	5.07
53	84.32	16.99	575.0	0.677	3.010	74.4	74.6	4.45
5	83.67	17.26	575.7	0.682	3.072	74.2	73.6	4.50
15	84.16	16.99	575.1	0.691	3.010	73.9	74.4	4.36
83	83.60	19.06	574.7	0.701	3.468	73.6	73.7	4.95
32	84.11	14.68	574.4	0.705	2.840	73.5	73.9	4.03
67	83.07	22.20	575.2	0.711	3.799	73.3	73.4	5.34
57	83.42	18.76	575.0	0.720	3.233	73.0	73.4	4.49
34	83.38	15.30	575.3	0.723	2.865	72.9	72.8	3.96
76	82.77	22.95	575.3	0.725	3.925	72.8	73.0	5.42
74	83.24	18.01	574.6	0.726	3.335	72.8	72.9	4.59
11	83.07	17.36	575.7	0.731	3.036	72.6	72.6	4.15
35	83.45	14.58	574.3	0.731	2.790	72.6	72.7	3.82
30	83.21	16.16	574.9	0.734	2.857	72.6	72.6	3.89
7	83.03	18.82	575.4	0.737	3.316	72.5	72.8	4.50
101	82.14	23.73	575.1	0.748	4.089	72.1	72.0	5.47
97	82.21	22.47	575.6	0.757	3.820	71.8	72.0	5.05
19	82.53	17.85	574.8	0.762	3.242	71.7	71.7	4.25
55	82.45	18.68	575.2	0.762	3.372	71.7	71.7	4.43
10	82.51	16.99	574.9	0.768	3.134	71.5	71.5	4.08
46	82.36	18.44	574.9	0.780	3.391	71.1	71.5	4.35
81	81.77	22.65	574.9	0.782	3.947	71.1	71.2	5.05
31	82.47	15.68	574.3	0.783	3.080	71.0	71.2	3.93
69	81.74	21.73	575.3	0.791	3.851	70.8	71.0	4.87
8	81.36	20.21	575.6	0.808	3.585	70.2	70.2	4.44
36	81.90	18.14	574.5	0.809	3.372	70.2	70.7	4.17
92	80.57	23.57	575.5	0.837	4.134	69.4	69.4	4.94
1	80.72	21.23	575.8	0.851	3.768	68.9	69.2	4.43
48	80.67	19.16	575.1	0.862	3.635	68.6	68.8	4.22
65	80.02	26.55	575.4	0.862	4.437	68.6	68.9	5.15
71	79.97	27.75	574.9	0.867	4.584	68.4	69.0	5.29
100	80.17	23.89	575.4	0.867	4.089	68.4	68.7	4.72
66	79.93	24.56	575.4	0.868	4.145	68.4	68.4	4.78
56	79.95	22.60	575.5	0.888	3.936	67.8	68.1	4.43
91	79.71	24.24	575.4	0.893	4.271	67.7	68.0	4.78
87	79.41	24.91	575.4	0.905	4.318	67.3	67.6	4.77
39	79.64	19.94	575.3	0.912	3.655	67.1	67.1	4.01
84	78.51	26.92	575.5	0.929	4.584	66.6	66.4	4.93
37	79.22	20.77	575.2	0.931	3.820	66.6	66.6	4.10
13	78.42	27.41	575.4	0.942	4.547	66.2	66.3	4.83
20	78.66	24.72	575.4	0.946	4.318	66.1	66.3	4.56
45	78.94	21.01	575.2	0.947	3.915	66.1	66.1	4.13
85	77.92	25.95	575.8	0.975	4.486	65.3	65.2	4.60
96	77.53	29.26	575.7	0.979	4.935	65.2	65.1	5.04
54	78.00	24.48	575.5	0.986	4.283	65.0	65.1	4.34
9	77.78	23.68	576.1	1.013	4.101	64.2	64.6	4.05
90	76.81	30.87	575.9	1.018	5.086	64.1	64.2	5.00
58	76.68	26.38	575.7	1.051	4.750	63.2	63.2	4.52
47	76.37	24.53	575.4	1.068	4.559	62.7	62.3	4.27
75	75.88	30.78	575.9	1.078	5.157	62.4	62.6	4.78
102	75.59	31.82	575.8	1.092	5.376	62.0	62.2	4.92
99	75.25	32.45	575.9	1.107	5.346	61.6	61.8	4.83
38	75.78	20.32	575.2	1.135	4.056	60.9	60.6	3.57
95	74.14	33.63	576.4	1.141	5.467	60.7	60.1	4.79
2	74.84	27.00	576.1	1.163	4.841	60.1	60.2	4.16
3	74.23	28.10	576.1	1.192	4.949	59.4	59.3	4.15
77	73.75	33.47	576.0	1.192	5.638	59.4	59.4	4.73
89	73.62	32.23	576.3	1.194	5.498	59.3	59.0	4.60
68	72.45	34.09	576.5	1.269	5.719	57.4	57.3	4.51
49	72.63	32.42	576.0	1.280	5.498	57.1	57.3	4.30
80	70.52	38.43	576.4	1.352	6.383	55.4	54.7	4.72
79	65.94	42.45	577.0	1.637	7.328	48.9	47.6	4.48

mm. thickness. The transmittancies, on the basis of a concentration of 1 gram of dry substance in 1 ml. of solution, and of 1-mm. thickness, were plotted against wave lengths.

Smooth curves were obtained, three of which are shown in Figure 1, for samples 38, 66, and 70 (Table I). The brightness, purity, and dominant wave length were calculated, as described in detail in (*5*) and the results of this monochromatic analysis are shown in the second, third, and fourth columns of Table I. The absorbancy indexes for wave lengths 560 and 420 mμ are given in the next two columns. A comparison between columns 2 and 5 shows that, as with the refined sugars, the brightness decreases in nearly the same order as the absorbancy index at 560 mμ increases. There is no such relationship between the brightness and the absorbancy index at 420 mμ; although the a values increase in a general way as the brightness decreases, there are large fluctuations up or down. The significance of these differences is discussed below.

Lorge and associates (*3*) fitted a multiple regression equation to the data, and obtained the following equation for the relationship between the absorbancy index at 560 mμ and the color computed by monochromatic analysis:

$$a, 560\ m\mu = -0.05373\ \text{brightness} - 0.00402\ \text{purity} - 0.00352\ \text{dominant wave length} + 7.30264 \quad (1)$$

The correlation coefficient for this equation is 0.9981, much better than for the corresponding equation for refined sugars (*5*). The equation also shows that the relative contribution of the purity and the dominant wave length is much smaller than that of the brightness.

As the absorbancy indexes are logarithms, a still better correlation was to be expected, as before, between the transmittancy at 560 mμ and the color expressed by monochromatic analysis. The transmittancies observed had to be corrected to exactly 60.00 refractometric Brix (0.7719 gram of dry substance in 1 ml. of solution) because the filtered solutions had a slightly higher Brix owing to evaporation during filtration. The corrected observed transmittancies for a thickness of 2.46 mm. are shown in column 7 of Table I. Lorge computed the following equation for the relation between the observed transmittancy and the monochromatic analysis:

$$T, 560\ m\mu, 60\ \text{Brix}, 2.46\ \text{mm.} = 1.7119\ \text{brightness} + 0.1675\ \text{purity} + 0.0673\ \text{dominant wave length} - 111.2555 \quad (2)$$

The correlation coefficient for this equation is 0.9992, much higher than for Equation 1 and for the corresponding equation for refined sugars (*5*). The transmittancies calculated by this equation are shown in column 8 of Table I. The differences between the found and calculated values average 0.22% transmittancy for the 102 samples. They exceed 0.5% in only nine cases, and are over 1% in only one case. With this last exception, they are well within the limit of error of transmittancy measurements in the range of 65 to 90% transmittancy.

Table II. Correlation between Absorbancy Index or Transmittancy at 560 Mμ and Brightness, Purity, and Dominant Wave Length

	Brightness	Purity	Dominant Wave Length
a, 560 mμ	0.9975	0.9391	0.8062
T, 560 mμ, 60 Brix, 2.46 mm.	0.9981	0.9362	0.8067

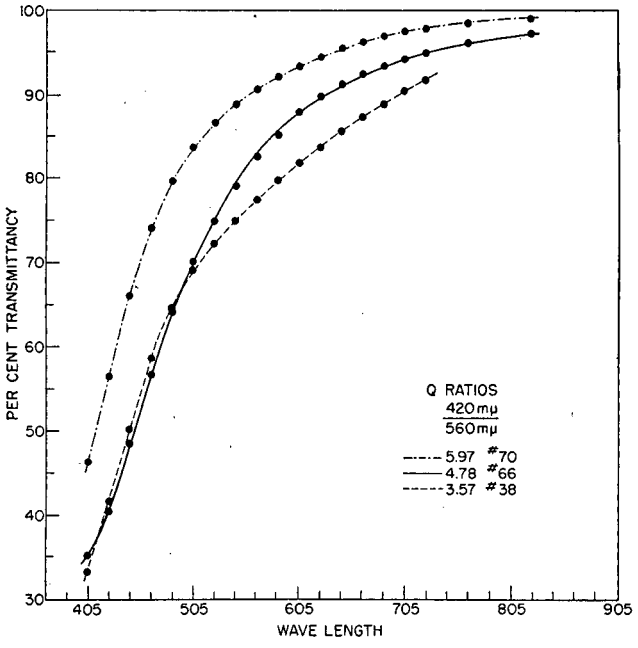

Figure 1. Transmittancy Curves of Three Raw Sugars

It is interesting to note the correlation coefficients between the absorbancy index and the transmittancy at 560 mμ on the one hand, and the brightness, purity, and dominant wave length on the other, as recorded in Table II.

In spite of the fact that the dominant wave length varies only between 573.3 and 577.0, there is nevertheless a fairly high correlation between it and the absorbancy index or the corresponding transmittancy at 560 mμ.

The higher correlation coefficients of Equations 1 and 2 for raw sugars, as compared to those previously found for refined sugars, are accounted for by the fact that the transmittancies of the refined sugar solutions were measured at the greatest available thickness, 5 cm. They were, therefore, in the range of 90 to 100% at 560 mμ, except for the six darkest sugars, and were affected by relatively greater observational errors. This strengthens the conclusion reached by the writers and other investigators that cells of at least 20-cm. thickness should be used for refined sugars, to have the readings fall within the most precise range between 30 and 60 or 70% transmittancy.

The sum total of the different coloring matters in refined sugars generally has higher *Q*-ratios 420 mμ/560 mμ (*5*) than in raw sugars (Table I, column 9), denoting a higher proportion of individual yellowish coloring matters. This is confirmed by the higher purity at equal brightness, as shown in Figure 2, in which the circles denote the average purity for seven successive groups of 10 samples each of the 70 refined sugars, and triangles denote the average purity for six successive groups of 15 samples each, followed by the group of the last 12 samples of the 102 raw sugars. The refined sugars have throughout a higher purity at equal brightness than the raw sugars.

The *Q*-ratios 420 mμ/560 mμ, given in Table I, column 9, also explain why the absorbancy index at 420 mμ bears little relation to the actual color, as perceived by the eye. They vary from 3.57 to 5.97, differing as much as 167%.

To cite an example of what this means, the absorbancy index of sugar 66 (Table I and Figure 1) at wave length 420 mμ is 2.2% higher than that of No. 38, while that at wave length 560 mμ, equivalent to the actual color, is 30.8% lower. The same is true for refined sugars, as noted from Table II of (*5*). The absorbancy index at 420 mμ of sugar 59 is only 0.5% higher than that of No. 84, but at wave length 560 mμ it is 43% higher, and the "color" determined by the method of Gillett, Meads, and Holven (*1*) is 123% higher. Similar examples can be found in the same tables.

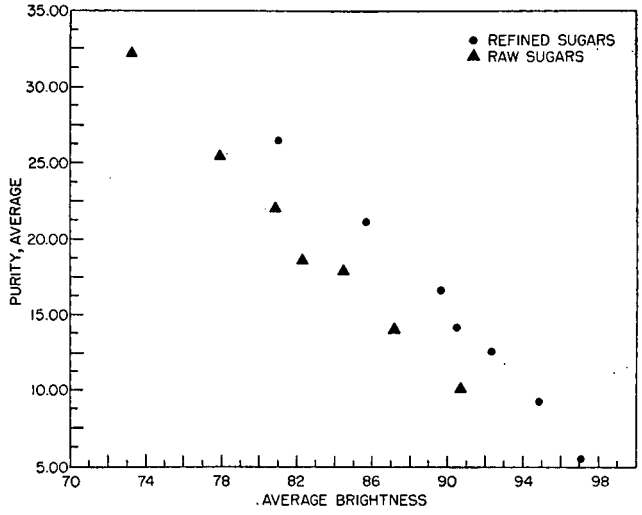

Figure 2. Purity *vs.* Brightness of Raw Sugar Solutions

This proves beyond doubt that the color, as perceived by the eye, and its chemical corollary, color concentration, cannot be determined by transmittancy measurements at the blue end of the spectrum or at any wave length substantially different from 560 mμ, but can be found accurately only at this particular wave length.

ACKNOWLEDGMENT

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Determination of Antimony by Radioactivation

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Slow neutron activation and radiochemical separations have been used to determine very small concentrations of antimony in samples of pure materials. The generalized technique of radioactivation analysis and the precautions that must be taken for the irradiation are given. Sensitivities of 1 part in 10^9 are attainable and the determination is capable of excellent accuracy. Methods of calculating the amount of activity formed by a neutron irradiation and of checking the radiochemical purity of the isolated radioelement are discussed.

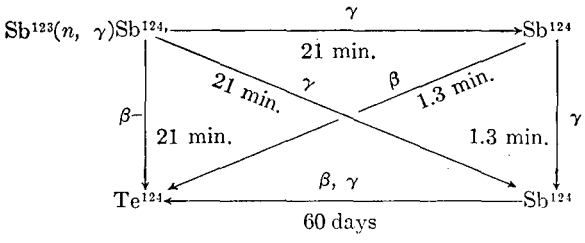
THE activation of the stable elements by a high intensity neutron source as a method of determining small concentrations of various elements is a technique that has come into prominence as a result of the construction of large uranium graphite reactors. Neutron intensities of 4×10^{12} neutrons per second per square centimeter (*4*) are available and the limit of detection is approximately 10^{-8} or 10^{-9} gram of the element sought per gram of the major constituent. The limit of detection is determined by the intensity of the neutron beam to which the sample is exposed, by the cross section, and by the length of time to which the sample is exposed to the neutron beam.

Radioactivation as a method of analysis was first used by Hevesy and Levi (*17*), and Seaborg and Livingood (*25*) used the cyclotron as a source of the activating particles. Numerous papers describing the technique and setting forth its potentialities have been published (*2, 5–7, 12, 13, 28*).

Naturally occurring antimony is made up of two isotopes, one of mass 121 (57.25%) and one of mass 123 (42.75%) (*29, 30*). When these isotopes are subjected to a neutron bombardment five radioactive isomers are formed. These isomers are produced by the reactions

$$Sb^{121}(n, \gamma)Sb^{122} \xrightarrow[3.5\ \text{min.}]{\gamma} Sb^{122} \xrightarrow[2.8\ \text{days}]{\beta,\ \gamma} Te^{122} \qquad (1)$$

(*8, 10, 19, 21, 29*)



(2)

(*10, 18, 29*)

After a short time has elapsed, the only nuclides that remain are the 2.8-day and the 60-day antimony isotopes, in addition to the other radioactive isotopes which may be formed by a neutron activation of other impurities or of the major constituent of the sample.

The total quantity of antimony 122 or antimony 124 activities formed as a result of a given neutron irradiation may be calculated from the equation (*26*)

$$A = (\sigma)(f)(N)(1 - e^{-\lambda t})$$

where A is the activity of the isotope in units of atoms disintegrating per second, σ is the thermal neutron cross section of the parent atom in units of 10^{-24} sq. cm. (barns), f is the neutron flux in units of neutrons per second per square centimeter, N is the number of atoms of the parent isotope exposed to the neutron flux, λ is the decay constant $\left(\frac{Ln2}{\text{half-life}}\right)$ of the isotope formed, and t is the length of time the sample remained in the neutron flux. A more useful form of the equation can be derived by including in the equation a factor that combines the known constants and the known thermal neutron cross sections of Sb^{121} (6.8 barns) (*27*) and of Sb^{123} (2.5 barns) (*27*) for the production of the 2.8-day Sb^{122} and the 60-day Sb^{124} isotopes, respectively, the accurately known isotopic abundances for the naturally occurring element, and the equation for the decay of the 2.8-day and 60-day isotopes. The equation

$$A_T = W(f)\left[\frac{(1 - e^{-\lambda_1 t_2})(e^{-\lambda_1 t_2})}{51.6} + \frac{(1 - e^{-\lambda_2 t_1})(e^{-\lambda_2 t_2})}{191}\right]$$

is obtained. In this equation A_T is the total number of antimony atoms disintegrating per unit time, W is the weight in grams of naturally occurring antimony exposed to the neutron flux, f, λ_1 is the decay constant of the 2.8-day isotope, λ_2 is the decay constant of the 60-day isotope, t_1 is the length of time the sample was exposed to the neutron flux, and t_2 is the length of time that elapsed between the cessation of bombardment and the radioactivity determination.

The activity of either of the two important antimony isotopes can be made to predominate at the time the sample is removed from the neutron flux by a proper selection of the irradiation time. In Figure 1 the amount of Sb^{122} and Sb^{124} radioactivity present after an irradiation time, t_1, is given. These curves also make possible an estimation of the "sensitivity" of the method. It is evident that for the bombardment of gram quantities of the major constituent a few thousandths of a part per million of antimony could be detected.

MONITORING OF NEUTRON FLUX

One of the most important problems of radioactivation analysis is the determination of the intensity of the neutron flux to which the sample has been exposed. This problem may be solved by a careful calibration of the neutron source, by irradiating a sample of known cross section at the same time that the unknown sample is irradiated, or by irradiating a sample of antimony with the unknown sample. In the latter case the antimony in the sample may be counted at the same time that the antimony monitor is counted, and a simple proportion for calculating the concentration of the antimony in the sample may be used.

In samples in which the major constituent has a large absorption cross section, a correction for the decrease of the neutron beam intensity toward the center of the sample must be made. The correction to be applied is calculated from the expression (*26*):

$$f = f_o(e^{-\sigma N x X})$$

where f is the flux of neutrons (neutrons/cm.$^{-2}$/second) after

passing through a thickness X of the material having a cross section σ. N_x is the density of the material in atoms per cc. The importance of this correction factor is decreased as the physical dimensions of the sample are decreased and for very small samples the correction factor can usually be neglected entirely. By integrating this equation between the limits o and X and dividing by X the average flux to which the sample was exposed can be obtained. For a capsule 0.5 cm. in diameter containing antimony metal powder, the calculated average flux is 99+% of the flux to which the sample was exposed.

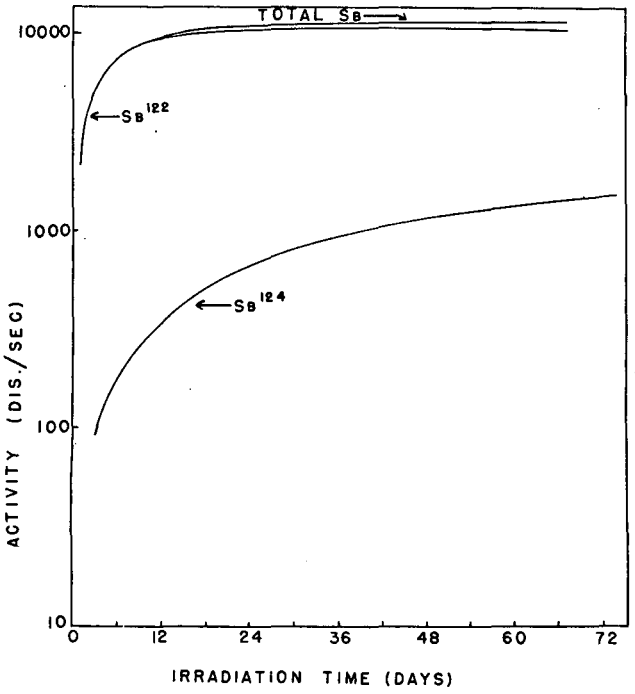


Figure 1. Amount of Antimony Radioactivity Present after Irradiation of t_1 Days

Disintegration rates shown were calculated for irradiation of 1 of antimony of natural isotopic composition in a flux of 5 × 10^{11} neutrons per second per sq. cm.

The antimony (metal) used to monitor the neutron beam is held at a known distance from the unknown sample by making use of a simple irradiation capsule which has been devised for this purpose or by careful spacing of the sealed quartz capsules in the irradiation can. The aluminum capsules are fabricated from pure aluminum (Aluminum Corp. of America designation 2-S) in order to minimize the attenuation of the neutron flux by the sample capsule. The capsules are shown in Figure 2.

Irradiation capsules may be easily fabricated from quartz tubing by sealing the ends after the sample has been introduced. The cross section of silica compares favorably with that of aluminum and less time is required to fabricate the capsule. The irradiation of several samples in the same irradiation can must be carried out after a careful placement of the capsules, as the flux distribution in the can may be heterogeneous and thus the probability that one sample might receive a higher intensity neutron bombardment than the other samples is increased.

The antimony must usually be chemically separated from other sample constituents before a radioactivity determination is made. Boldridge and Hume (*3*) separated antimony from other sample constituents by precipitation of the metal with chromous chloride, precipitation of antimony pyrogallate, and precipitation of antimony(III) with cesium chloride, presumably as $Cs_3Sb_2Cl_9$. Each of these compounds was found to be a suitable weighing form, although the greatest accuracy was obtained with the pyrogallol and chromous chloride methods. L. C. Nelson, of the New Brunswick Laboratory, used the chromous chloride precipitation method as a substitute for the sulfide precipitation and the electrolysis steps given in the procedure below with excellent results. Antimony has been separated as stibine (*1, 9, 14, 15, 23, 24*). However, interference by arsenic, selenium, and several other metals is serious. Maxwell *et al.* (*20*) separated carrier-free antimony from a tin cyclotron target by using a combination of sulfide precipitations and a distillation with hydrobromic acid. The distillation of antimony as the chloride and bromide and electrolytic precipitations are classical methods of separation (*31*). Edwards and Voigt studied the isopropyl ether extraction of antimony(V) as the chloride (*11*).

The number of different types of chemical separations which must be performed to separate antimony from other radioelements formed in the irradiation is determined by the concentration, cross section, and decay characteristics of the other elements as well as the specificity of the chemical separations used. Because the zirconium oxide samples used to test the procedure (Table I) contained appreciable quantities of elements whose chemistry is similar to that of antimony, a more complicated separation procedure than is usually necessary was used. Distillation of antimony trichloride followed by a precipitation (by electrolysis or chromous chloride) of antimony metal is usually sufficient to prepare the sample for counting.

CHEMICAL PROCEDURE

Wash the sealed quartz capsule containing the zirconium oxide (~0.5 gram) with a 10% hydrochloric acid solution containing a few drops of hydrofluoric acid, and after rinsing with distilled water break the capsule under 50 ml. of concentrated sulfuric acid. Add to the sulfuric acid–zirconium oxide mixture an aliquot of antimony trichloride solution containing the equivalent of 100 mg. of antimony ion. Allow the mixture to stand until the solution of the zirconium oxide is complete. Transfer the solution to a 100-ml. volumetric flask and dilute to the mark with sulfuric acid.

Rinse into the distillation apparatus (*31*) 1 gram of hydroxylamine hydrochloride and 20 mg. each of arsenic and tin chlorides, with a minimum amount of hot distilled water. Transfer 10 ml. of the zirconium oxide sample solution to the distillation flask, and rinse the walls of the dropping funnel with a 10 ml.-volume of concentrated sulfuric acid. During the addition of the sample and rinse solutions, cool the flask with water.

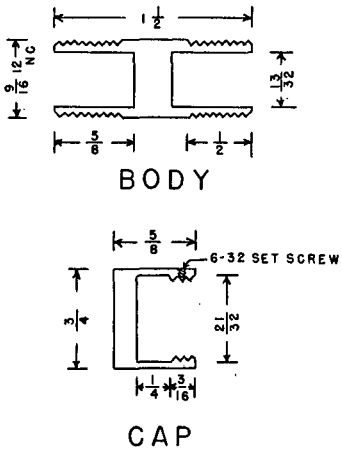


Figure 2. Aluminum Irradiation Capsule

Dimensions in inches

Add 125 ml. of distilled water slowly, heat the contents of the distilling flask to 150° C., and start carbon dioxide bubbling through the solution. Add 20 ml. of concentrated hydrochloric acid through the funnel and collect the antimony trichloride distillate over the temperature range 155° to 165° C.

After the completion of the distillation the distillate should be approximately 7 *M* in hydrochloric acid. Oxidize the antimony to the pentavalent form by adding dropwise a saturated solution of potassium permanganate. Equilibrate 50 ml. of peroxide-free isopropyl ether with an equal volume of 7 *M* hydrochloric acid solution, discard the aqueous layer and, using two 25-ml. aliquots of the ether solution, extract the pentavalent antimony into the isopropyl ether. The addition of catechol (50 mg. per liter of ether) to the stock solution of isopropyl ether will prevent oxidation (*22*) and subsequent loss of antimony caused by this effect.

Combine the organic phases and place in a large separatory funnel. Add 35 ml. of distilled water and 2 drops of 12 *M* hydro-

Table I. Analyses of Zirconium Oxide Samples

(Parts per million)

Sample No.	Sb Added	Sb Found	Al, Fe, Zn Added	Bi, Co, Cr, Cu, Mg, Ni, Pb, Sn Added	As, Mn, P, Si, V, Ti, Mo Added	Ag, B, Be, In Added
2692	10	10.7	133	10	100	1.0
2693	5	5.6	67	5	50	0.5
2694	2	2.5	26	2	20	0.2
2695	1.0	1.5	13	1	10	0.1
2696	0	0.54	0	0	0	0

chloric acid. Completely evaporate the isopropyl ether by attaching a water aspirator to the top of the funnel and opening the stopcock until a steady stream of air is drawn through the solution.

Make the solution 2 *M* in hydrochloric acid, heat to 90° to 100° C., and bubble hydrogen sulfide gas through the solution for 10 to 15 minutes. Collect the precipitate on a 42 Whatman filter paper or a sintered-glass filter funnel. Wash the precipitate with a 25- to 30-ml. portion of hydrogen sulfide-saturated distilled water and with a like volume of distilled water.

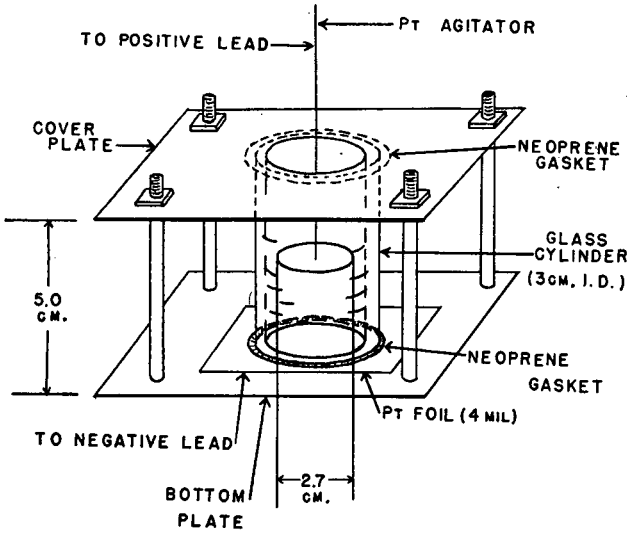


Figure 3. Cell for Electrodeposition of Antimony

Transfer the antimony to the electrolysis cell (Figure 3) by washing the precipitate from the funnel into the cell with 20 ml. of sodium sulfide solution containing 140 mg. of sodium sulfide per ml. Add 15 ml. of distilled water and 0.75 gram of potassium cyanide and deposit the antimony by passing a current of 50 ma. (1.3 to 1.5 volts) through the cell for 2 hours.

Wash the deposited antimony with distilled water and with ethyl alcohol, dry the deposit for 10 minutes at 80° C. (constant weight), and determine the weight of the antimony metal.

DETERMINATION OF ANTIMONY RADIOACTIVITY

The antimony radioactivity was determined by using a bell-type thin end-window Geiger-Müller counter tube attached to a commercial scaler (Nuclear Instrument and Chemical Corp. Model 163). As all samples were compared to antimony metal irradiated under identical irradiation conditions, the problems attendant to determinations of absolute disintegration rates were eliminated.

TREATMENT OF THE NEUTRON FLUX MONITOR

The antimony activity in the monitor is determined in a manner analogous to the sample radioactivity determination. In most cases the separation of antimony activity from gross sample impurities is unnecessary and the chemical steps include only a solution of the monitor in hydrochloric acid, addition of a known amount of antimony carrier solution, precipitation of antimony sulfide, and electrolysis of the antimony as given in the procedure above. As a correction for chemical yield is made for the monitor in the same manner as that for the unknown sample, the small errors caused by the electrodeposition cancel. [Antimony analyses have been reported by Henz (*16*) to yield results consistently high by 1.5 to 2% of the total antimony.] If the antimony concentration in the carrier solution is determined by using the electrodeposition procedure, the errors in the chemical yield determination may be cancelled by those cases in which an antimony monitor is not used.

The use of an antimony monitor to serve as a check on the neutron intensity of the neutron source also serves the purpose of compensating for long-term variations in counter efficiency, of obviating the necessity of determining accurately the correction factors for the geometry of the counting arrangement, the back-scattering of beta-rays from the material on which the sample is mounted, and the self-scattering and/or self-absorption by the sample precipitate, since the weight of antimony precipitate on the counting disk is nearly the same for the antimony monitor as for the unknown sample.

RESULTS

The synthetic samples used to test the method were prepared by adding known amounts of antimony to a pure zirconium oxide powder. As the synthetic samples were prepared for the use of the New Brunswick Laboratory spectrographic group, a large number of other elements were also added in known quantities (Table I). The presence of these elements served as a test of the specificity of the method.

The synthetic samples shown in Table I received a 2-week irradiation in the Oak Ridge National Laboratory pile. This irradiation was sufficient to yield a specific antimony 124 radioactivity of approximately 500 disintegrations per second per microgram or a total antimony radioactivity of approximately 10,000 disintegrations per second per microgram. As the antimony was isolated from a small part (50 mg.) of the total irradiated sample and most of the 2.8-day antimony 122 had decayed by the time the chemical separations were performed, the counting rates observed were from 1 to 30 counts per second for the series of samples. The observed counting rates could have been increased to from 20 to 600 counts per second by separating the antimony from other sample constituents immediately after the samples were removed from the pile. For samples containing a smaller concentration of antimony the aliquot size could also be increased.

The results given in Table I indicate that the original zirconium oxide contained 0.5 p.p.m. of antimony. It is unlikely that results consistently high by this constant amount could be caused by errors in the counting rate determination or in the chemical yield determination, or by contamination from external sources, for these errors would be observed either as constant multipliers or as erratic additions. The recovery of added antimony carrier does not usually influence the accuracy of the method, as a correction for losses is applied and the losses are usually less than 20% of the inactive antimony added.

The energy of the radiations from each of the isolated antimony metal precipitates was determined by absorption curve methods as an additional check of the efficiency of the separations. The beta and gamma-ray energies found by feather analysis or half-thickness determinations checked the values given by Way *et al.* (*29*).

ACKNOWLEDGMENT

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for the preparation of the synthetic samples of zirconium oxide used to test the procedure.

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Analysis of Mixtures of Dicobalt Octacarbonyl and Cobalt Carbonyl Anion

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A study of the hydroformylation (oxo) process in this laboratory required the analysis of mixtures containing both dicobalt octacarbonyl, $[Co(CO)_4]_2$, and cobalt carbonyl anion, $[Co(CO)_4]^-$, the latter being present either as cobalt hydrocarbonyl, $HCo(CO)_4$, or as a cobalt salt. Because no method was available for this purpose, the authors devised the present procedure. The two-step method depends on the decomposition of all carbonyls, by treatment with iodine, to yield carbon monoxide; and the selective precipitation of the anion by nickel *o*-phenanthroline chloride, followed by decomposition of the precipitate with liberation of carbon monoxide. As the determination is based on a gasometric procedure, it is suited for the analysis of mixtures, such as those from the hydroformylation reaction, which may contain cobalt salts and metallic cobalt.

MOST of the mechanisms that have been proposed (*1*, *9*) for the hydroformylation (oxo) reaction involve the postulation that the homogeneous catalyst is either dicobalt octacarbonyl or cobalt hydrocarbonyl, but no method for the determination of these carbonyls in the reaction products has yet been devised. The dark solution of aldehydes, ketones, and alcohols that is removed from the reaction vessel often contains cobalt not only as dicobalt octacarbonyl, cobalt hydrocarbonyl, cobalt salts of the hydrocarbonyl, and cobalt salts of organic acids, but also as finely divided metal (attracted by a magnet). In the course of an investigation in this laboratory, it became desirable to devise a simple and rapid method for the accurate determination of dicobalt octacarbonyl, $[Co(CO)_4]_2$, and cobalt hydrocarbonyl, $HCo(CO)_4$, in the mixtures usually obtained in the hydroformylation reaction.

In a study of these carbonyls (*3*, *4*) it was shown that dicobalt octacarbonyl is quantitatively decomposed by bromine in glacial acetic acid or iodine in benzene according to Equation 1 (*3*).

$$[Co(CO)_4]_2 + 2I_2 \longrightarrow 2CoI_2 + 8\overline{CO} \qquad (1)$$

Although the decomposition of the free cobalt hydrocarbonyl by halogens is not described in the literature, Hieber and Teller (*6*) mention that excess iodine in benzene decomposes cadmium cobalt carbonyl, $Cd[Co(CO)_4]_2$, quantitatively into the corresponding metal halides and carbon monoxide.

An aqueous solution of nickel *o*-phenanthroline chloride has been used by Hieber and coworkers for the quantitative determination of cobalt hydrocarbonyl in aqueous (*5*) and ammoniacal solution (*4*). It should be emphasized that this reagent is not specific for the acid, $HCo(CO)_4$, but rather for the cobalt carbonyl anion, $[Co(CO)_4]^-$.

OUTLINE OF METHOD

The present method is based on the following facts: Dicobalt octacarbonyl, cobalt carbonyl anion, and cobalt hydrocarbonyl are quantitatively decomposed by excess iodine according to Equations 1, 2, and 3.

$$2[Co(CO)_4]^- + 3I_2 \longrightarrow 2CoI_2 + 8\overline{CO} + 2I^- \qquad (2)$$

$$2HCo(CO)_4 + 3I_2 \longrightarrow 2CoI_2 + 8\overline{CO} + 2HI \qquad (3)$$

The amount of carbon monoxide evolved serves as a measure of the total amount of carbonyl (dicobalt octacarbonyl and cobalt carbonyl anion) present.

Nickel *o*-phenanthroline cation does not react with dicobalt octacarbonyl. With cobalt carbonyl anion, however, a salt is formed according to Equation 4.

$$2[Co(CO)_4]^- + [Ni(o\text{-}Phthr)_3]^{++} \longrightarrow [Ni(o\text{-}Phthr)_3][Co(CO)_4]_2 \quad (4)$$

This salt is insoluble in water and in hydrocarbon solvent such as hexane or toluene and may, therefore, be separated from dicobalt octacarbonyl, which is readily soluble in these solvents. The freshly precipitated nickel *o*-phenanthroline salt of cobalt hydrocarbonyl is quantitatively decomposed by excess iodine according to Equation 5.

$$[Ni(o\text{-}Phthr)_3][Co(CO)_4]_2 + 3I_2 = [Ni(o\text{-}Phthr)_3]I_2 + 2\,CoI_2 + 8\overline{CO} \quad (5)$$

The amount of carbon monoxide evolved serves as a measure of the amount of cobalt carbonyl anion present.

The difference between the amount of cobalt carbonyl anion and the total amount of carbonyl (dicobalt octacarbonyl and cobalt carbonyl anion) is equivalent to the amount of dicobalt octacarbonyl present.

REAGENTS AND APPARATUS

Iodine Solution. Add water to 300 grams of potassium iodide and 50 grams of iodine to make 1000 ml. of solution. Take 40 ml. of this solution for samples containing 0.0 to 0.6 gram of total carbonyl.

Nickel *o*-Phenanthroline Chloride Solution (*4*). Dissolve 2.8 grams of *o*-phenanthroline monohydrate and 1.2 grams of nickel chloride hexahydrate in 100 ml. of water. Use 25 ml. of this solution for samples containing 0.00 to 0.25 gram of cobalt carbonyl anion.

Apparatus. The apparatus used has been described (*8*). The gas buret has a capacity of 450 ml. The reaction vessel is a 125-ml. Erlenmeyer flask (*7*) fitted with a ground-glass joint and a side arm provided with a stopcock for the addition of the iodine solution.

PROCEDURE

Pipet a suitable aliquot of the solution to be analyzed into the Erlenmeyer flask, add enough toluene to bring the volume of the solution to about 40 ml., attach the flask to the apparatus, and purge the system with nitrogen or (preferably) carbon monoxide. Stir the solution 1 to 2 minutes, and record the volume of gas. Add 40 ml. of the iodine solution through the side arm, and stir the solution vigorously until no more gas is evolved (usually 10 to 15 minutes). Record the final volume.

Pipet a second aliquot into a glass-stoppered Erlenmeyer flask containing 25 ml. of the nickel *o*-phenanthroline chloride solution and 25 ml. of benzene. Shake the flask vigorously for about 1 minute; add about 30 ml. of water and 1 ml. of 6 *N* hydrochloric acid solution; shake again, and allow to stand for about 1 hour. Filter with suction through a rapid filter paper; wash with benzene and finally with water. Dissolve the precipitate in about 40 ml. of pyridine and transfer the solution to the reaction vessel. Attach the reaction vessel to the apparatus, purge the system with nitrogen (or carbon monoxide), and decompose the pyridine solution with 40 ml. of iodine solution as described above. Calculate the weights of total carbonyl or of precipitated cobalt carbonyl anion as follows:

$$\text{Grams of } Co(CO)_4 = \frac{\text{ml. of gas evolved (NTP)} \times 0.171}{89.6}$$

DISCUSSION OF METHOD

The importance of protecting dicobalt octacarbonyl and cobalt carbonyl anion from prolonged exposure to oxygen is illustrated by the following experiments.

When a benzene solution of dicobalt octacarbonyl was stirred in an atmosphere of oxygen for 3 hours, a dark precipitate formed, and gas corresponding to 40% of the available amount of carbon monoxide was evolved, consisting of carbon monoxide and carbon dioxide in a ratio of 4 to 1. When a benzene solution of dicobalt octacarbonyl was stirred in an atmosphere of nitrogen, 12% of the available carbon monoxide was evolved in 5 hours. An aqueous solution of known cobalt carbonyl anion content prepared from dicobalt octacarbonyl and ammonia (*4*) was stored for several days in an atmosphere of nitrogen without change. On exposure to air, however, the solution decomposed within a few minutes with discoloration and evolution of gas.

Table I. Analyses of Blends

Sample	% $[Co(CO)_4]_2$ Calcd.	% $[Co(CO)_4]_2$ Found	% $[Co(CO)_4]^-$ Calcd.	% $[Co(CO)_4]^-$ Found
1	20.2	20.6	79.8	79.4
2	20.2	18.6	79.8	81.4
3	55.4	56.4	44.6	43.6
4	58.4	59.2	41.6	40.8
5	71.3	70.4	28.7	29.6
6	73.7	72.8	26.3	27.2
7	84.9	83.4	15.1	16.6

The solution of iodine in aqueous potassium iodide reacts smoothly and quantitatively. This reagent is easily made up in any desired concentration, presents no handling problem, possesses excellent storage properties, and thus has obvious advantages over a solution of bromine in glacial acetic acid (*3*).

That cobalt hydrocarbonyl reacts with iodine according to Equation 3 to give HI and not H_2 according to Equation 6

$$2HCo(CO)_4 + 2I_2 \longrightarrow H_2 + 2\,CoI_2 + 8\overline{CO} \quad (6)$$

was shown by the following experiment.

A freshly prepared sample (*2*) of approximately 0.2 gram of cobalt hydrocarbonyl dissolved in 20 ml. of toluene was decomposed with excess iodine. Mass spectrometric analysis of the evolved gas showed that carbon monoxide and hydrogen were present in a ratio of 300 to 1. If the decomposition had followed Equation 6, the ratio of carbon monoxide to hydrogen should have been 8 to 1. The traces of hydrogen probably originated from some decomposition of the cobalt hydrocarbonyl (Equation 7) prior to the reaction with iodine.

$$2HCo(CO)_4 \rightleftharpoons H_2 + [Co(CO)_4]_2 \quad (7)$$

Although cobalt carbonyl anion may be determined gravimetrically (*4*) by weighing the precipitated nickel *o*-phenanthroline salt of cobalt hydrocarbonyl (Equation 4), the authors have found that this salt can be quantitatively decomposed according to Equation 5. This reaction makes possible the rapid and accurate determination of cobalt carbonyl anion by a gasometric method. It is important to carry out the decomposition with the freshly precipitated salt. Analyses of precipitates that had been allowed to stand overnight in a vacuum desiccator gave only 80 to 90% of the theoretical amount of carbon monoxide. The nickel *o*-phenanthroline salt of cobalt hydrocarbonyl often separates as an oil that is easily emulsified. Acidification with hydrochloric acid, however, causes the formation of a crystalline precipitate that can be readily filtered.

ANALYTICAL RESULTS

In order to test the present method, solutions of known amounts of dicobalt octacarbonyl and cobalt carbonyl anion (*4*) were prepared. The blends had a total carbonyl content of about 0.6 gram per 10 ml. and varied in cobalt carbonyl anion content from 79.8 to 13.9%. The results of the analyses of these blends are listed in Table I.

The method is well suited for the determination of small amounts of carbonyl and may readily be adapted to micro procedures because 89.6 ml. of carbon monoxide are evolved by 1 millimole (0.171 gram) of carbonyl.

In general, the strict precautions observed in working with carbon monoxide should be practiced in working with the cobalt carbonyls. Dicobalt octacarbonyl has a low vapor pressure and there is little danger of inhaling its vapor. Cobalt hydrocarbonyl has a high vapor pressure and may be very toxic, but, in the absence of an atmosphere of carbon monoxide, it starts to decompose well below room temperature into hydrogen and dicobalt octacarbonyl. The apparatus used in the analytical determinations was placed in a large well ventilated room with an exit tube leading to the hood for venting carbon monoxide. The hydrocarbonyl was prepared in a hood.

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Nonorthophosphate Contaminant of Neutron-Irradiated Rock Phosphates

Procedures for Its Removal

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Orthophosphate compounds, upon irradiation with slow (thermal) neutrons, yield a radioactive product, the P^{32} content of which is only partly in the orthophosphate condition. The compounds are therefore not suited for tracer experiments without treatment to convert all the P^{32} to the orthophosphate form. Calcium phosphates tested showed a considerable amount of nonorthophosphate P^{32}, depending partially upon conditions of irradiation. A method is presented for determining nonorthophosphate P^{32} in calcium phosphates. A treatment is shown that will result in an irradiated rock phosphate suitable for plant investigations. This work should impress users of neutron-irradiated compounds with the frequency of occurrence of this phenomenon. The presence of more than one radioactive isotope, if not noted and eliminated by conversion or compensation, invalidates tracer experiments. An important fertilization material, rock phosphate, can now be used in tracer experiments.

SLOW (thermal) neutron irradiation of orthophosphate compounds, no matter how pure they may be, yields a radioactive product, the P^{32} content of which is only partly in the orthophosphate condition. The nonorthophosphate, presumably produced as a consequence of the recoil of the P^{32} nucleus from gamma-ray emission as it passes to the ground state, has been identified as phosphite in irradiated alkali phosphates (*4*, *6*, *8*) and as hypophosphate in irradiated calcium phosphates (*3*). The possible presence of P^{32} in more than one form in irradiated samples necessitates a careful examination of any irradiated phosphate that is to be used as a source of radioactive phosphorus in tracer experiments. The basic requirement for a proper label is that all the P^{32} in the labeling compound be in, or readily convertible to, the same form as the phosphorus compound to be labeled.

Recent work in this laboratory (*2*) points to pyrophosphate as the dominant form of nonorthophosphate in the irradiated potassium dihydrogen phosphate distributed by the Oak Ridge National Laboratory—the P^{32} source used extensively in late years by this bureau for labeling phosphate fertilizers for greenhouse and field experiments (*5*). Moreover, it was found that the labeling processes provide conditions favorable to the reconversion of the nonorthophosphate, so that the labeled fertilizers carry an insignificant amount of it. The same end could probably be attained in any labeling process involving synthesis of a compound.

On the other hand, the introduction of P^{32} into a natural material, such as phosphate rock, which cannot be synthesized in the laboratory, must be accomplished by direct irradiation of the material. As the irradiated rock must be utilized directly as the tracer source, a nonorthophosphate content is a serious drawback (*4*). Phosphate rock is used extensively (more than 800,000 short tons in 1949) for direct application to the soil, and thus considerable interest attaches to the measurement of its effectiveness as a source of phosphorus in the growing of vegetation with the aid of the radioactive tracer technique. Looking to this end, a study was made of the amount and distribution of nonorthophosphate in irradiated phosphate rock, and of treatments that might be used to destroy the nonorthophosphate without seriously altering the properties of the rock. Results of this study are reported here.

PHOSPHORUS SPECIFIC ACTIVITY AND NONORTHOPHOSPHATE CONTENT OF SOME IRRADIATED CALCIUM PHOSPHATES

In the spring of 1950 eight calcium phosphates and a sample of potassium acid phosphate were irradiated in the neutron pile at Oak Ridge under various conditions of neutron flux and temperature. Samples of each of the nine materials were exposed to a high neutron flux with an intermediate (water-cooled) temperature, a low neutron flux with a low temperature, or a high neutron flux with a high temperature. These samples, after irradiation, were returned to the laboratory and phosphorus specific activity and nonorthophosphate content were determined (Table I).

It can be seen from Table I that a great part of the phosphorus activity in neutron-irradiated calcium phosphates may exist as a nonorthophosphate contaminant. The nonorthophosphate content in each case was higher in the calcium phosphates than in

Table I. Nonorthophosphate Content of Phosphates Irradiated under Selected Conditions

Phosphate	Irradiation Treatment [a]	Total Specific Activity [b], Relative Units	Nonorthophosphate: % of total P^{32}	Nonorthophosphate: Days after irradiation
KH_2PO_4	A	0.364	18.31	39
	B	0.561	26.69	22
	C	1.650	0.57	22
Florida land pebble	A	0.362	48.28	40
	B	0.526	48.86	23
	C	1.549	31.01	23
Curacao rock	A	0.340	46.33	41
	B	0.518	52.51	24
	C	1.504	30.33	24
Hydroxylapatite	A	0.349	37.65	104
	B	0.511	40.46	87
	C	1.534	37.46	87
Morocco rock	A	0.378	29.52	105
	B	0.565	41.27	88
	C	1.570	18.83	88
Steamed bone	A	0.394	31.51	146
	B	0.567	36.42	129
	C	1.502	31.04	129
Fluorapatite	A	0.365	34.59	146
	B	0.515	37.73	129
	C	1.420	26.72	129
Tricalcium phosphate	A	0.416	51.78	146
	B	0.564	48.45	129
	C	1.567	42.79	129
Phosphate glass	A	0.367	37.97	146
	B	0.533	33.49	129
	C	1.357	31.33	129

[a] Treatment A. High neutron flux, intermediate temperature (water-cooled). Irradiation period, April 24 to May 5, 1950.
Treatment B. Low neutron flux, low temperature. Irradiation period, 4 weeks beginning April 24, 1950.
Treatment C. High flux, high temperature. Irradiation period, 4 weeks beginning April 24, 1950.
[b] Results corrected to activity of June 13, 1950.

Table II. Observed Half-life of Nonorthophosphate Activity

Phosphate	Observed Half-life, Days
KH_2PO_4	13.5
Florida land pebble	14.6
Curacao rock	14.2
Hydroxylapatite	14.0
Morocco rock	13.6
Steamed bone	13.9
Fluorapatite	13.6
Tricalcium phosphate	13.6
Phosphate glass	14.9

the potassium acid phosphate. The phosphorus specific activity of all materials for each treatment was not significantly different. Treatment differences in specific activity were due to the short time of irradiation in Treatment A and to the differences in neutron flux between Treatment B and Treatment C.

Half-life determinations on the activity given by the nonorthophosphate fractions of the irradiated phosphates indicated that the activity was due to P^{32} (Table II).

The exact forms of the nonorthophosphate have not yet been determined. However, analysis using manganese chloride at pH 4.2 as a precipitant (*2*) showed 16 to 30% of the nonorthophosphate in irradiated phosphate rock to be pyrophosphate.

Investigating further the nonorthophosphate content and phosphorus specific activity of irradiated calcium phosphates, four samples of phosphate rock (Florida land pebble) were sealed in quartz ampoules under vacuum, and under atmospheres of argon, air, and oxygen, respectively. These samples then were irradiated and later analyzed for nonorthosphosphate content and phosphorus specific activity. The results of the determinations on the four samples are given in Table III. There appeared to be no significant differences in the phosphorus specific activities of the four samples, although there was some variation in the nonorthophosphate content. Apparently, under the above conditions, there was no large effect on the nonorthophosphate content due to the differences in atmosphere during irradiation.

Table III. Nonorthophosphate Content and Phosphorus Specific Activity of Phosphate Rock

(Irradiated in vacuum, argon, oxygen, and air)

Sample	Treatment	Nonorthophosphate, % of Total P^{32}	Total Phosphorus Specific Activity, Relative Units
1	Sealed in vacuum	29.26	1.370
2	Sealed in atmosphere of oxygen	31.66	1.439
3	Sealed in atmosphere of argon	34.36	1.413
4	Sample ignited and sealed in atmosphere of air	38.59	1.400

ELIMINATION OF NONORTHOPHOSPHATE CONTAMINANT OF NEUTRON-IRRADIATED ROCK PHOSPHATES

It has been shown that neutron-irradiated calcium phosphates possess a radioactive phosphorus contaminant which is not of the ortho form. To make these materials suitable for radioisotope studies it is necessary to convert the nonorthophosphate P^{32} to the orthophosphate form. Experiments on irradiated phosphate rock have been performed with this goal in mind. The irradiated phosphate rock was treated in various manners in an effort to reduce the nonorthophosphate content to a negligible amount without changing the physical or chemical properties of the rock under various treatments involving heat, pressure, and moisture.

After each decontamination treatment, nonorthophosphate content and specific activity were determined, either by dissolving the entire sample and determining the average nonorthophosphate content and specific activity, or by performing a stepwise dissolution with dilute acid, followed by determination of the nonorthophosphate content and specific activity in each extract. Any changes in the distribution of the nonorthophosphate content or specific activity could be observed by the use of the latter procedure.

The various treatments and the results of decontamination treatments on a sample of irradiated phosphate rock (Florida land pebble, sample C, Table I) are given in Table IV.

Of the procedures listed in Table IV, only Treatment 9, where the irradiated phosphate rock was heated in air at 500° for 91 hours, was successful in reducing the nonorthophosphate content to an insignificant amount without altering the material. Heating at lower temperatures for even longer periods failed to decontaminate the phosphate rock as successfully. Bomb treatments substantially reduced the nonorthophosphate content, but alteration of the material was observed at the 300° and 350° C. heat treatments. Alteration was indicated by the formation of a

Table IV. Effect of Decontamination Treatments on Irradiated Phosphate Rock [a]

Treatment No.	Description	Nonorthophosphate, % of Total P^{32}
1	Check	27.5
2	Heated in water at 90° C. for 3 hours	18.2
3	Heated in water at 90° C. for 6 hours	24.5
4	Heated at 200° C. for 91 hours, sealed in bomb with water present	16.2
5	Heated at 300° C. for 91 hours, sealed in bomb with water present [b]	7.0
6	Heated at 350° C. for 91 hours, sealed in bomb with water present [b]	4.3
7	Heated at 200° C. for 91 hours, dry at atmospheric pressure	22.3
8	Heated at 200° C. for 241 hours, dry at atmospheric pressure	17.5
9	Heated at 500° C. for 91 hours, dry at atmospheric pressure	1.6

[a] Florida land pebble phosphate rock, sample C, Table I.
[b] Phosphate rock altered by treatment.

Table V. Distribution of Nonorthophosphate Contaminant and Phosphorus Specific Activity in Neutron-Irradiated Phosphate Rock[a]

(As shown by stepwise dissolution analysis)

Extract No.	Dissolved P^{31}, % Total P^{31}	Specific Activity, Relative Units	Nonorthophosphate, % of Total P^{32}
1	2.8	1.474	6.2
2	3.1	1.250	8.9
3	3.1	1.188	12.2
4	3.1	1.133	12.6
5	3.1	1.141	15.3
6	3.1	1.148	15.2
7	3.1	1.160	13.7
8	3.0	1.085	15.1
9	3.0	1.078	14.4
10	3.0	1.102	17.0
11	2.0	1.122	17.3
12	2.9	1.137	17.5
13	63.8	...	....

[a] Phosphate rock sample, Treatment 8, Table IV.

siliceous crust, both inside and outside the glass sample container, which when analyzed was found to contain 1.58% fluorine. A petrographic examination of the treated samples also revealed an increase in refractive index of the phosphate (examination made by J. G. Cady).

The typical data of Table V were obtained by analyzing a sample of neutron-irradiated phosphate rock by the stepwise dissolution technique. In treatments for the elimination of nonorthophosphate contaminant, stepwise dissolution analysis showed that it was reduced to its lowest amount in the initial extracts and either remained the same or gradually increased in the succeeding extracts. Phosphorus specific activity showed that the distribution of P^{32} in the irradiated phosphate rock was uniform, except that there was a slightly higher concentration in the initial extracts—a condition that points to a concentration of the P^{32} in the surface layers of the particles. Half-life determinations and aluminum absorption measurements on the radiations from these initial extracts showed that the radiations were not different from the radiations of the succeeding extracts and that the radiations were due to P^{32}.

Additional decontamination experiments were attempted on another sample of irradiated phosphate rock (Florida land pebble, sample 2, Table III). The treatments involved heating of the phosphate rock in the presence of steam at atmospheric pressure for 48 and 168 hours, respectively. The results of the treatments are shown in Table VI. Almost complete decontamination was accomplished by the 450° C. heat treatment for 168 hours. Chemical and petrographic examination of the treated samples showed that no great chemical or physical alterations had occurred in the material due to the treatment. This product would be suitable for phosphate investigations with plants.

Chemical and petrographic analysis of the phosphate rock samples before and after various decontamination treatments are given in Table VII.

Table VI. Decontamination of Irradiated Phosphate Rock[a] by Heating at 450° C. in Steam at Atmospheric Pressure

Treatment No.	Description	Nonorthophosphate, % of Total P^{32}
10	Check	31.66
11	48 hours	7.20
12	168 hours	1.93

[a] Florida land pebble phosphate rock, sample 2, Table III.

Table VII. Composition of Phosphate Rock after Nonorthophosphate Decontamination Treatments

Treatment No.	Treatment	Citrate-Insoluble P_2O_5, %	CO_2, %	F, %	Petrographic Examination[a]
1	Check	32.67	1.50	3.75	
4	Heated at 200° C. for 91 hours, sealed in bomb with water present	....	....	....	No alteration noticeable
5	Heated at 300° C. for 91 hours, sealed in bomb with water present	....	....	3.50	Alteration indicated by formation of siliceous crust and increase in refraction index
6	Heated at 350° C. for 91 hours, sealed in bomb with water present	....	....	....	Alteration indicated by formation of siliceous crust and increase in refraction index
9	Heated at 500° C. for 91 hours, dry at atmospheric pressure	31.73	1.54	3.56	No alteration noticeable
..	Heated at 450° C. for 168 hours in steam at atmospheric pressure	32.85	1.55	3.43	No alteration noticeable

[a] Petrographic examinations made by J. G. Cady.

DETERMINATION OF NONORTHOPHOSPHATE CONTENT

Reagents. Hydrochloric Acid, 3 *N*. Dilute 250 ml. of concentrated hydrochloric acid (37.6%) to 1 liter.

Ammonium Molybdate. Add 111.6 grams of MoO_3 to 500 ml. of water. Slowly add 110 ml. of concentrated ammonium hydroxide (specific gravity 0.90) with constant stirring. Filter and dilute to 1 liter.

Ammonium Nitrate, 5% solution. Dissolve 50 grams of ammonium nitrate in 500 ml. of water. Dilute to 1 liter.

Sodium Dihydrogen Phosphate, 2 mg. of phosphorus per ml. Dissolve 8.91 grams of sodium dihydrogen phosphate monohydrate in 500 ml. of water. Dilute to 1 liter.

Hydrogen Ion Exchange Resin. Make a slurry of a cation exchange resin (Amberlite IR-100) with 3 *N* hydrochloric acid and allow to stand for several hours with occasional mixing. Decant the liquid and add fresh 3 *N* hydrochloric acid, repeating this process several times. Finally decant the supernatant liquid and wash the resin with water until free of hydrochloric acid. Add enough water to cover the resin and store for future use.

Nitric Acid, reagent grade, 70% (specific gravity 1.42).

Ammonium Nitrate, reagent grade crystals.

Preparation of Hydrogen Ion Exchange Resin Column. Irradiated phosphate rock contains radioactive cations, calcium and iron, which are conveniently separated from the radioactive phosphorus by passing the solution of the sample through a cation exchange column.

Place a wad of glass wool in the bottom of a 50-ml. buret and add 30 ml. of the hydrogen ion-exchange resin. Wash the column with water until the wash water is neutral.

To regenerate the column after use, back-wash the column with water and then regenerate the resin by passing 500 ml. of 3 *N* hydrochloric acid through the column at a rate of 10 ml. per minute. Wash with water until the wash water is neutral. The column is then ready for use again. Collect all solutions coming from the column during regeneration and washing and handle as radioactive liquid wastes of calcium and iron.

Procedure. For each sample of irradiated rock phosphate dissolve approximately 25 mg. of the sample in 30 ml. of cold 0.1 *N* nitric acid. Pass 25 ml. of this solution through the hydrogen ion-exchange resin column at a rate of 10 ml. per minute. Collect the effluent liquid in a 100-ml. volumetric flask and wash the column with water until the total effluent volume is 100 ml. Designate this solution, which is free of all radioactive cations, as assay solution I.

Take a 75-ml. aliquot of assay solution I and transfer to a 250-ml. beaker. Add 5 ml. of the sodium dihydrogen phosphate solution and then dissolve 15 grams of ammonium nitrate in the solution. Add 10 ml. of concentrated nitric acid, then 25 ml. of the ammonium molybdate reagent with stirring. Allow the solution to stand for 30 minutes. Stir occasionally during that time, and decant the supernatant liquid through a Whatman No. 42 filter into a 200-ml. volumetric flask. Wash the precipitate several times by decantation with 5% ammonium nitrate solution.

To the combined filtrate and washings in the 200-ml. volu-

metric flask, add concentrated ammonium hydroxide until the solution is alkaline to phenolphthalein. Allow to cool to room temperature and dilute to volume with water. Designate this solution, which contains the nonorthophosphate contaminant, as assay solution II.

Dissolve the ammonium phosphomolybdate precipitate left in the beaker and filter in 1 N ammonium hydroxide and discard as P^{32} waste.

Take a 5-ml. aliquot of the cation-free assay solution I and make up to a volume of 200 ml. with 0.1 N nitric acid. Designate this solution as assay solution III. This solution contains the total P^{32} activity of the irradiated phosphate.

Count assay solutions II and III to 10,000 total counts by the use of a solution counter. Calculate the nonorthophosphate content as a percentage of the total P^{32} activity from the following equation:

$$\text{Nonorthophosphate \% of total } P^{32} = \frac{\text{counts per second on solution II}}{\text{counts per second on solution III}} \times 100$$

DETERMINATION OF TOTAL PHOSPHORUS

Colorimetric P^{31} determinations were made on assay solution I by the ammonium metavanadate procedure proposed by Mission (*7*) and also used by Barton (*1*) in the analysis of the phosphate rock. Nonorthophosphate is not measured by this procedure, but its conversion to orthophosphate may be effected by boiling in an oxidizing acid solution. This is not necessary, however, because the substance is carrier-free and the weight of nonorthophosphate, like that of the total P^{32} complement, is negligibly small in comparison with the total phosphorus.

Reagents. Nitric Acid, 7.5 N. Ammonium Metavanadate. Dissolve 2.345 grams of ammonium metavanadate in 500 ml. of hot water, add 10 ml. of nitric acid (specific gravity 1.42), and dilute the solution to 1 liter.

Ammonium Molybdate. Dissolve 90 grams of ammonium molybdate tetrahydrate in 500 ml. of warm water (50° C.) containing 10 ml. of ammonium hydroxide (specific gravity 0.90). Filter and dilute to 1 liter.

Procedure. Pipet an aliqout of assay solution I into a 50-ml. volumetric flask. This aliquot should contain between 50 and 300 micrograms of phosphorus and should not be more than 25 ml. If the aliquot is less than 25 ml., dilute to 25 ml. with water. Add 10 ml. of 7.5 N nitric acid, mix well, and add 5 ml. of ammonium metavanadate reagent. Mix well and add 5 ml. of the ammonium molybdate reagent. Dilute to volume with water and mix well. Allow the color to develop for 0.5 hour and then read on a suitable colorimeter using a 420 mμ filter. Convert to micrograms of P^{31}, using a calibration curve prepared by the above procedure on known amounts of phosphorus. Calculate micrograms of P^{31} per milliliter of assay solution III by the use of the dilution factor.

DETERMINATION OF TOTAL PHOSPHORUS SPECIFIC ACTIVITY

The activity of assay solution III per unit of P^{31} present is a measurement of the phosphorus specific activity of the irradiated sample. A unit of P^{31} may be expressed as micrograms of P^{31} per milliliter of assay solution III.

Procedure. Count assay solution III to 10,000 counts with the use of a solution counter. Calculate the specific activity by dividing by the micrograms of P^{31} per milliliter of assay solution III.

Comments on Procedure. The degree of accuracy attainable in the determination of specific activity by the above procedure was investigated. Four separate samples of an irradiated sample were taken and specific activity measurements made. The counting technique was investigated by making two 10,000 total counts on each solution and also by repeating the counting on three separate days. From the results (Table VIII) it appears that a variation of as much as $\pm 2.5\%$ may be expected in specific activity measurements determined by this procedure.

STEPWISE DISSOLUTION MEASUREMENTS

In studying the radioactive phosphorus distribution within neutron-irradiated calcium phosphates, a stepwise dissolution was performed on the materials by successive extractions with dilute acid. Analysis of each extract for nonorthophosphate content and phosphorus specific activity then gave information on the distribution of the nonorthophosphate contaminant and the amount of radioactive phosphorus in each of the extractable layers of the irradiated phosphates.

Reagents. Nitric acid extracting solutions, 0.001 N, 0.005 N, 0.01 N, and 0.1 N.

Procedure. Transfer a sample (50 to 200 mg.) of the irradiated calcium phosphate to a 15-ml. conical-shaped centrifuge tube, and extract it successively with 10-ml. portions of dilute acid. Upon each addition of the dilute acid, stir the mixture with a glass rod for 2 minutes and then centrifuge for 10 minutes. Decant the clear supernatant liquid after each extraction into a prepared hydrogen ion-exchange resin column. Pass each extract through a column at a rate of 10 ml. per minute collecting the effluent liquid in a 100-ml. volumetric flask. Wash the column with water until the total effluent volume is 100 ml. Analyze each extract for nonorthophosphate content and specific activity as described above.

Comments on Procedure. The practice of making eleven or twelve extractions on the irradiated material with dilute acid, extracting about 2 to 3% of the total phosphorus in each extract and then dissolving the remainder of the sample in 0.1 N acid, is usually followed. The sum of the phosphorus in all solutions is taken as the total phosphorus in the sample.

Table VIII. Reproducibility Attainable in Determination of Specific Activity

No. of Replicates	Date Counted	Average Deviation from Mean, %		
		Activity	P^{31}	Specific activity
4	11/20	0.58	0.90	1.32
4	11/22	1.08	0.90	2.00
4	11/24	0.41	0.90	2.50

The percentage of the total phosphorus dissolved by each extraction depends upon the size of the sample and the amount of acid present. The time of each extraction was standardized at 2 minutes. In the course of these investigations it was necessary to vary the size of sample and acid concentration so as to obtain extracts that had moderate amounts of P^{32} activity present. As the specific activity of an irradiated sample decreased through decay, the use of larger samples was necessary. Sample weights varied from 50 to 200 mg. Concentrations of the acid extracting solutions varied from 0.001 N to 0.01 N, higher acid concentrations being necessary with the larger samples of material in order to extract the desired 2 to 3% of the total phosphorus.

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Preparation of the samples and arrangements for their irradiation were carried out by Maurice Fried of this bureau.

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Volumetric Methods for the Assay of Amidines

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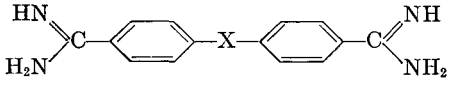
Lately, especially in Europe, many organic amidines are finding use in therapeutics. Researches are being carried on in many laboratories to find newer and more effective amidine derivatives. Existing methods for assaying these compounds and determining their molecular weights are too elaborate and require costly apparatus. Two simple volumetric methods, one iodometric in an alkaline medium and one mercurimetric, have been developed. The composition, characters, and structure of the iodamidines obtained in the assay as well as the new mercury derivatives, the mercuriamidines, from the mercurimetric method were determined.

THE aromatic amidines used in medicine have the following general structure (*4*):



in which —X— can be either a double bond stilbene link, —CH=CH—, or a polymethylene chain with or without oxygen atoms, such as $-(CH_2)_n-$ or $-O-(CH_2)_n-O-$.

New volumetric methods were developed and applied successfully to the assay of the following amidines:

1. Lomidine dimethane sulfonate, pentamidine, or diamidine M. (4,4′-diamidino-1,5-diphenoxypentane methane sulfonate)—($C_{21}H_{32}O_8N_4S_2$), molecular weight = 532.6.
2. Lomidine diisethionate—($C_{23}H_{36}O_{10}N_4S_2$), molecular weight = 592.7.
3. Hexamidine diisethionate (4,4′-diamidino-1,6-diphenoxyhexane diisethionate)—($C_{24}H_{38}O_{10}N_4S_2$), molecular weight = 606.7.
4. Benzamidine hydrochloride—($C_7H_{13}O_2N_2Cl$), molecular weight = 192.6.
5. *p*-Sulfamidobenzamidine (base)—($C_7H_9O_2N_3S$), molecular weight = 199.2.
6. Stilbamidine diisethionate (*p,p′*-diamidinostilbene diisethionate)—($C_{20}H_{28}O_8N_4S_2$), molecular weight = 516.6.
7. 2-Hydroxystilbamidine diisethionate—($C_{20}H_{28}O_9N_4S_2$), molecular weight = 532.6.
8. *p*-Arsonobenzamidine (base)—($C_7H_9O_3N_2As$), molecular weight = 243.1.

IODOMETRIC DETERMINATION OF AMIDINES

Bougault and Robin (*1–3, 7–9*) have shown that on mixing solutions of sodium hydroxide iodine and amidine a yellow precipitate is obtained to which they gave the general name "iodamidine" and proposed the following formula and equation for its formation:

$$R—C(:NH).NH_2 + I_2 \longrightarrow HI + R—C(:NH).NHI \text{ or } R—C(:NI).NH_2 \quad (1)$$

The present author has tried this reaction on the previously mentioned amidines and worked out a procedure based on it for the volumetric assay of the amidines (Table I). The following facts were deduced from the numerous trials:

1. The reaction always takes place according to Equation 1. One molecule of iodine is consumed by every amidine group in the formula.
2. The precipitation of the iodamidine is very rapid.

In acidic, neutral, or slightly alkaline media (pH < 8.5) the precipitate is dark red-brown in color and very bulky. It consists of the corresponding iodamidine adsorbing superficially a large quantity of free iodine. The amount of adsorbed iodine increases irregularly with the acidity of the medium.

When the medium is alkaline, or rendered so after precipitation in an acidic medium, the precipitate turns pale yellow and is finely crystalline. The sodium hydroxide interacts with the free as well as with the adsorbed iodine, leaving the iodamidine in a pure insoluble state and of a definite composition:

$$R—C(:NI).NH_2$$

3. The iodamidine of an amphoteric amidine, such as *p*-sulfamidobenzamidine or 2-hydroxystilbamidine, is soluble in alkalies and the method cannot be applied to it.

Table I. Iodometric and Mercurimetric Determinations of Amidines

	Equivalent Weight	*E*, Gram
Iodometric Determination		
Lomidine methane sulfonate	Mol. wt. / 4	0.006658
Lomidine diisethionate	Mol. wt. / 4	0.007408
Hexamidine diisethionate	Mol. wt. / 4	0.007584
Benzamidine hydrochloride[a]	Mol. wt. / 2	0.004816
Stilbamidine diisethionate	Mol. wt. / 4	0.006457
Mercurimetric Determination		
Lomidine methane sulfonate	Mol. wt. / 4	0.002663
Lomidine diisethionate	Mol. wt. / 4	0.002963
Hexamidine diisethionate	Mol. wt. / 4	0.003033
p-Sulfamidobenzamidine base	Mol. wt. / 4	0.000996
Stilbamidine diisethionate	Mol. wt. / 4	0.002583
2-Hydroxystilbamidine diisethionate	Mol. wt. / 4	0.002662
p-Arsonobenzamidine base	Mol. wt. / 3	0.00162

[a] An accurately weighed small sample of the amidine is to be added to the blank titration. Precipitation requires higher alkalinity, add 10 ml. of 30% sodium hydroxide.

Principle of the Method. The amidine is precipitated with an excess of iodine, and rendered alkaline, and the residue is separated by filtration. The filtrate is acidified and the iodine that is not consumed by the amidine is liberated and titrated with standard thiosulfate.

The equivalent weight is equal to the molecular weight of the product divided by double the number of amidine groups in the formula. The precision and accuracy of the iodometric method are illustrated in Table II.

Reagents.

0.1 *N* iodine, U.S.P.
0.05 *N* sodium thiosulfate solution
2 *N* sodium hydroxide solution
2 *N* hydrochloric acid solution
Starch test solution, U.S.P.

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Procedure. The amidine is dried over sulfuric acid for 4 hours. A sample of about 0.06 gram, accurately weighed, is introduced into a glass-stoppered 100-ml. volumetric flask and dissolved in 15 to 20 ml. of distilled water. (If the product consists of the insoluble amidine base, it is dissolved by using a few drops of dilute phosphoric acid.) Then 25 ml. of 0.1 *N* iodine solution are added, followed by 20 ml. of 2 *N* sodium hydroxide solution. The mixture is shaken well, diluted to exactly 100 ml. with distilled water, and filtered through a dry filter into a dry beaker. The first 25 ml. of the filtrate are rejected.

An accurately measured 50-ml. aliquot portion of the filtrate is introduced into an Erlenmeyer flask and neutralized with 2 *N* hydrochloric acid (about 20 ml. of the acid are required), 1 ml. of the acid is added in excess, and the liberated iodine is titrated with 0.05 *N* sodium thiosulfate solution, using starch test solution as indicator.

A blank titration is conducted at the same time, using all the reagents but without adding the amidine.

If the iodamidine is slightly soluble in water it is necessary to include in the blank titration a small accurately weighed sample (about 0.01 gram) of the amidine.

Calculation.

$2 \times (V' - V) \times E$ = grams of amidine in sample S (or in $S - S'$)

where V = milliliters of 0.05 *N* thiosulfate used for 50-ml. aliquot portion of filtrate in assay
V' = milliliters of 0.05 *N* thiosulfate used for 50-ml. aliquot portion of filtrate in blank determination
S = grams of dried amidine taken in assay
S' = grams of amidine introduced into the blank titration if iodamidine is slightly soluble in water, otherwise $S' = 0$
E = grams of pure amidine equivalent to 1 ml. of 0.05 *N* thiosulfate (see Table I for the values of E)

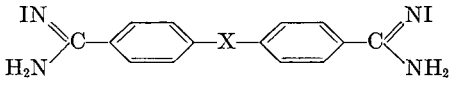
Properties of the Iodamidines. The iodamidines occur as fine pale yellow crystalline powders, soluble in alcohol and in dilute acids, and hydrolyzable in water, liberating, in all cases, free iodine which can be titrated with standard thiosulfate. They decompose when heated to 127° to 132° C. Treated with hydrochloric acid and water they react as follows:

$$R{-}C(:NI).NH_2 + HCl + H_2O = R{-}C(:NH).NH_2.HCl + HIO$$

Treated with water, hydrochloric acid, and potassium iodide they liberate double their content of free iodine.

$$R{-}C(:NI).NH_2 + HCl + KI = R{-}C(:NH).NH_2 + KCl + I_2$$

The residues were dried over sulfuric acid and under reduced pressure (8 to 10 mm.) and were analyzed for their nitrogen and iodine content. The analyses gave results that agree with the following suggested structure:



MERCURIMETRIC DETERMINATION OF AMIDINES

At room temperature and a pH between 5.2 and 7.0, mercuric acetate interacts with the amidines to form voluminous gelatinous white insoluble derivatives which the author named "mercuriamidines." Under these conditions the reaction runs quantitatively to the right and it was applied to the volumetric determination of the amidines. The reaction is:

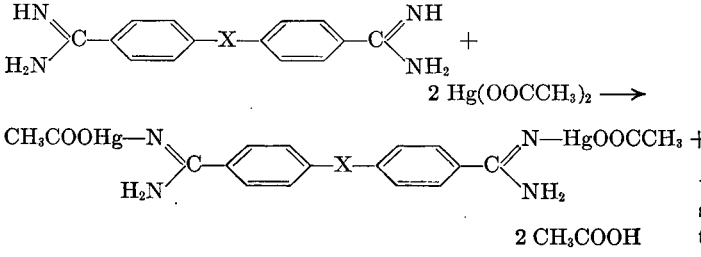


Table II. Precision and Accuracy of Iodometric and Mercurimetric Determinations of Amidines

	Sample Taken for Assay, Gram	Av. Values Found, Mean Gram.	Av. Deviation from Mean Precision	Av. Accuracy Based on Weighed Sample
Iodometric Determination				
Lomidine methane sulfonate	0.0507	0.0501	0.0002 = 4/1000	12/1000
Lomidine diisethionate	0.0645	0.0638	0.0005 = 8/1000	11/1000
Hexamidine diisethionate	0.0560	0.0554	0.0006 = 11/1000	10/1000
Benzamidine hydrochloride	0.0737	0.0738	0.0002 = 3/1000	1.3/1000
Stilbamidine diisethionate	0.0484	0.0478	0.0004 = 8/1000	12/1000
Mercurimetric Determination				
Lomidine methane sulfonate	0.0500	0.0489	0.0004 = 8/1000	22/1000
Lomidine diisethionate	0.0649	0.0645	0.0003 = 4.6/1000	6/1000
Hexamidine diisethionate	0.0592	0.0594	0.0005 = 8.4/1000	3.3/1000
p-Sulfamidobenzamidine	0.0431	0.0426	0.0002 = 4.7/1000	11/1000
Stilbamidine diisethionate	0.0488	0.0490	0.0004 = 8/1000	4/1000
2-Hydroxystilbamidine diisethionate	0.0462	0.0463	0.0006 = 13/1000	2/1000
p-Arsonobenzamidine base	0.0575	0.0566	0.0005 = 9/1000	15/1000

The best and most stable solution to be used is a 0.1 *N* mercuric acetate solution buffered with crystalline sodium acetate.

Reagents.

0.1 *N* buffered mercuric acetate solution (*5*). Dissolve 15.9 grams of ACS mercuric acetate and 34.0 grams of sodium acetate in 1000 ml. of water.
0.02 *N* ammonium thiocyanate solution
Sodium acetate, U.S.P. reagent
Ferric ammonium sulfate test solution, U.S.P.
Nitric acid, concentrated, U.S.P. reagent

On standing, the pH of the solution may drop to below 5.2. Then it is adjusted to pH 6.2 by adding 0.1 *N* sodium hydroxide solution drop by drop until a permanent yellow turbidity is formed and the mixture is filtered.

Procedure. An accurately weighed sample (about 0.06 gram) of the amidine powder, dried over sulfuric acid, is introduced into a 100-ml. glass-stoppered volumetric flask and dissolved in 20 ml. of distilled water. If the sample is the insoluble amidine base, it is dissolved in a few drops of dilute acetic acid and diluted with 20 ml. of water, one drop of phenolphthalein indicator solution is added, and the mixture is neutralized with 0.1 *N* sodium hydroxide. Then 25 ml. of the 0.1 *N* buffered mercuric acetate solution are added, followed by 3 grams of crystalline sodium acetate. The mixture is kept at 18° to 22° C. for 20 minutes and shaken from time to time. Finally the volume is completed with distilled water to exactly 100 ml., shaken very well, and filtered through a dry filter into a dry beaker. The first 15 ml. of the filtrate are rejected.

An accurately measured 50-ml. aliquot portion of the filtrate is transferred into an Erlenmeyer flask, and diluted with 25 ml. of water. Five ml. of concentrated nitric acid and 1 ml. of the ferric alum solution are added, and the mixture is cooled to 10° to 12° C. (*6*). and titrated with 0.02 *N* ammonium thiocyanate.

A blank determination is performed at the same time.

Calculation.

$2 \times (V' - V) \times E$ = grams of pure amidine in whole weighed sample

where V = milliliters of 0.02 *N* thiocyanate consumed by half of filtrate in assay
V' = milliliters of 0.02 *N* thiocyanate used for half of filtrate in blank determination
E = grams of pure amidine equivalent to 1 ml. of 0.02 *N* thiocyanate (see Table I for values of E)

Effect of Temperature. When the determination is performed at a temperature below 12° C., the results obtained are 5 to 6% below the correct values; at 28° C. and above, mercuration is increased and the results are about 10% higher. When the temperature reaches 40° C. yellow mercuric oxide begins to separate. The most accurate results are those obtained at room temperature (18° to 22° C.).

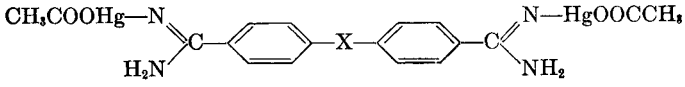
Effect of pH. The reaction of the medium has a great influence on the precipitation of the mercuriamidines. At pH 4 precipitation is partial and at pH 3.5 it may not take place at all. When the pH is 7 or above, mercuric oxide starts to separate and the results are irregularly increased.

Precipitation takes place quantitatively when the pH is kept between 5.2 and 7.0. It is most accurate at pH 6.2. The precision and accuracy of the method are shown in Table II.

Properties of the Mercuriamidines. The mercuriamidines are white, bulky, very gelatinous, and insoluble in water and in alcohol. They are dissolved by dilute acids.

Dried over sulfuric acid and under reduced pressure (8 to 10 mm.) they occur as white fine amorphous powders.

The precipitates dried over sulfuric acid under reduced pressure and analyzed for their mercury, nitrogen, and acetate content gave results that agree with the following suggested general structure:



CONCLUSION

These two methods or at least one of them can be used for the determination of the purity and of the molecular weights of the amidines.

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Application of Ion Exchange to Determination of Boron

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Conventional methods for the determination of boron require a rather lengthy separation from interfering elements. In an effort to improve this, an attempt was made to substitute ion exchange for the usual distillation. The method developed employs a cation exchanger to separate boron from large amounts of cation-forming elements. The measurement of the boron content, accomplished by a modification of the familiar titrimetric procedure in the presence of invert sugar, permits the presence of moderate amounts of such anions as silicate, arsenate, molybdate, and phosphate. The method gives accuracy equal to or better than conventional procedures in the analysis of a variety of types of samples with boron contents ranging from 0.03 to 20.0%. An appreciable saving in time is possible.

COLORIMETRIC, gravimetric, and volumetric methods of measuring boron concentration have been proposed, but their application to many materials received for analysis requires a difficult and frequently lengthy separation of the boron from interfering elements.

The most general method of separation involves distillation of boric acid as its methyl ester (*2*). When this separation is followed by a titrimetric determination, a blank of 0.3 mg. or less of boron is introduced, which is due in part to the extraction of boron from glassware and in part to a titration error. Incomplete volatilization is obtained from large amounts of aluminum salts and a double distillation is recommended in the presence of both iron and silicon. The time required for this procedure is a further disadvantage. Separation of boron from some elements which form weak bases has been attempted by precipitation of the hydrous oxides using various alkali or alkaline earth hydroxides, carbonates, or oxides. In all cases boron is adsorbed by the hydrous oxide precipitate and a reprecipitation is necessary except for very dilute solutions. Schafer and Sieverts (*6*) precipitated zinc, nickel, iron, and aluminum with 8-quinolinol without adsorption of boron. Electrolysis of boron solutions using a mercury cathode provides an excellent separation but does not remove aluminum, beryllium, titanium, zirconium, vanadium, arsenic, or phosphorus (*8*). Other less attractive methods, including an ether extraction, have been proposed.

Boric acid can be separated from interfering cations without many of the limitations and disadvantages of the above methods by employing the ion exchange technique for the removal of interfering ions. The proposed method involves passage of the neutral or slightly acid solution through a strong acid type of cation exchanger. After carbon dioxide has been removed from the effluent by boiling, the pH is adjusted to 6.90, invert sugar is added, and the boron-containing complex acid is titrated back to pH 6.90 with standard alkali.

REAGENTS

Standard boric acid solutions were prepared by dissolving weighed amounts of anhydrous boric oxide in water to give concentrations of 0.2 and 1.0 mg. of boron per milliliter, respectively. The boric oxide was prepared by fusion of reagent grade boric acid in a platinum dish.

Carbonate-free 0.1 *N* and 0.02 *N* sodium hydroxide solutions were prepared from saturated sodium hydroxide solution (*3*) and were standardized by potentiometric titration of aliquots of the standard boric acid solutions using the procedure described for the

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titration of samples. An unstandardized 2 *N* solution was also prepared for use in preliminary neutralization.

Invert sugar solution was prepared by the method of Mylius (*5*). Commercial sucrose (1 kg.) was dissolved in 650 ml. of previously boiled hot water and 8 ml. of 1 *N* hydrochloric acid were added. The solution was heated at 80° to 90° C. for 2 hours and then adjusted to pH 6.90 (measured electrometrically using a pH meter) with alkali just before use.

The following reagent grade salts were used to provide ions for testing the efficacy of the ion exchange separations: $AlCl_3.6H_2O$; $BeSO_4.H_2O$; MgO; ZnO; $CdSO_4.4H_2O$; $Co(NO_3)_2.6H_2O$; $CuSO_4.5H_2O$; $HgSO_4$; $NiSO_4.6H_2O$; $Th(NO_3)_4.4H_2O$; $SnCl_4.5H_2O$; $TiCl_4$; $UO_2SO_4.3H_2O$; $Zr(SO_4)_2.4H_2O$; $K_2Cr_2O_7$; $KMnO_4$; Na_3VO_4; $CrCl_3.6H_2O$; $MnCl_2.4H_2O$. $Fe_2(SO_4)_3.xH_2O$ and $Na_2O.xSiO_2$; were used after analyses to determine the iron and silicon contents, respectively.

APPARATUS

Both Dowex 50 and Amberlite IR-100 A.G. were found to provide a satisfactory separation of boric acid from interfering cations. Because Amberlite IR-100 was available in the analytical grade, it was used in all cases except when high capacity was required—viz., for samples weighing more than 1 gram. The resin columns were of the Jones reductor type, consisting of a tube terminated at the top with a reservoir of 75-ml. capacity and at the bottom with a stopcock and outlet tube. Two sizes were employed: 1.9 cm. (inside diameter) × 30 cm., 80-cc. capacity, and 2.6 cm. (inside diameter) × 33 cm., 175-cc. capacity. The resin columns were supported by 4-cm. plugs of tightly compressed glass wool. In order to effect economy of time and reagents it was found advantageous to replace the used resin with previously regenerated resin, so that a new sample could be analyzed immediately. The used resin was allowed to accumulate and was then transferred to a large column and regenerated with 10% hydrochloric acid until the effluent gave no test for the ions that had been adsorbed. After thorough washing the resin was stored for further use.

A Beckman Model H 2 line-operated pH meter was used in conjunction with a glass electrode and saturated calomel cell for the potentiometric titrations and for pH adjustment. The titration was carried out in a carbon dioxide–free atmosphere by using a Berzelius beaker (spoutless) as the titration vessel, and providing it with a stopper bored to receive the glass and calomel electrodes, the motor-driven stirrer, and an inlet tube for an air stream. The air stream had been passed through successive bottles of concentrated sulfuric acid, soda lime (two bottles), and water.

PROCEDURE

Samples of suitable size are dissolved in water or in a minimum amount of hydrochloric acid. When the application of heat is necessary to effect solution, the flask is connected to a reflux condenser to prevent loss of boron by volatilization. The solution is diluted to 50 ml. and is then passed through the resin bed. The resin is washed with 200 ml. of water in small portions. The rate of flow is adjusted so that the time for passage of the sample and washings is approximately 15 minutes. The effluent is nearly neutralized to methyl orange with 2 *N* sodium hydroxide and is boiled under a reflux condenser for 5 minutes. No volatilization of boron was apparent when the solutions were boiled gently in covered beakers, but a reflux condenser is a necessary precaution in case the time or rate of boiling is not carefully controlled. After cooling to room temperature in a water bath, the solution is adjusted to pH 6.90 with 0.02 *N* alkali. Sufficient invert sugar is then added to make the resulting concentration 0.6 *M* and the sample is titrated immediately to pH 6.90 with standard sodium hydroxide solution. The volume of standard alkali required to restore the solution to a pH of 6.90 after the addition of invert sugar is multiplied by the boron titer of the alkali to calculate the amount of boron present.

DISCUSSION

Titrimetric Determination. After boron has been isolated free of interfering substances by an ion exchange separation, the titrimetric and colorimetric procedures appear most attractive for measuring boron concentration. In general, colorimetric methods are more sensitive and selective and could undoubtedly be applied advantageously in many instances, especially when extremely small amounts of boron are to be measured. The titrimetric procedure was chosen for this work, however, because it is accurate and relatively rapid, does not require a preliminary evaporation of the effluate, and does not involve handling of hazardous concentrated sulfuric acid solutions. Boric acid is very weakly ionized, but the addition of certain polyhydric alcohols or large concentrations of calcium salts promotes the formation of stronger complex acids which can be titrated. As the pH of a 0.1 *N* boric acid solution is approximately 5, the interference of strong acids can be eliminated by preliminary neutralization to the methyl orange end point. This classical titration procedure has been modified by Foote (*1*) and Schafer and Sieverts (*7*), who titrated the boric acid solution to the same pH before and after the addition of a polyalcohol, thus eliminating the interference of weak acids and bases which were present in such small amounts that their buffering action was negligible. The principle involved is that with no polyalcohol present boric acid is so weakly ionized that it is only slightly neutralized at pH values up to 7.6, but in the presence of sufficient polyalcohol it is completely neutralized at or below this pH.

This modified type of titration was chosen for the determination of the boron concentration following an ion exchange separation because it did not necessitate the removal of small quantities of weak acids which are formed by elements such as sulfur, phosphorus, silicon, arsenic, and molybdenum. Small amounts of these anion-forming elements are present in many boron-containing metallurgical materials and are not separated from boron by means of a cation exchanger. The proposed titration procedure also eliminated inaccuracies due to variation in the small resin blank—i.e., a slight amount of residual acid washed out of the ion exchange column after the resin had been thoroughly rinsed. The adopted procedure represents a compromise between the modifications that had been proposed.

The apparent ionization constant of the complex boric acid increases with polyalcohol concentration and the pH at the titration equivalence point is thus dependent on this factor. It is desirable to have the polyalcohol concentration as high as possible, so that the equivalence point will come at a relatively low pH and the volume of standard alkali required for neutralization will then more nearly approach the theoretical value, as less boric acid is neutralized before addition of the polyalcohol. The polyalcohol concentration is effectively limited, however, by the volume of solution which accumulates during washing of the ion exchange column unless a time-consuming evaporation is included.

Investigation of the potentiometric titration curves for boric acid in the presence of varying concentrations of invert sugar showed that 0.6 *M* was a suitable concentration for invert sugar and in this medium the neutralization of boric acid was complete at a pH of 6.90. The slope of the curve at the equivalence point was 1.4 pH units per ml. and the volume of alkali required deviated from the theoretical value by less than 3%. This deviation was taken into account by standardizing the sodium hydroxide solutions against pure boric acid, using the procedure described for titration of the samples. The titration curve for boric acid without polyalcohol has a greater slope but is sufficiently parallel to the curve for boric acid in the presence of invert sugar to minimize errors due to possible pH meter drift.

Effect of Electrolytes. The apparent ionization constant of boric acid in aqueous solutions increases with boric acid concentration and with the concentration of certain ions such as lithium, barium, and calcium (*4*). The effect of electrolyte concentration variation on the accuracy of the titrimetric determination was therefore studied by titrating boric acid solutions containing known amounts of sodium chloride ranging up to a concentration of 0.25 *N*. The amounts of 0.02 *N* sodium hydroxide required for neutralization to a pH of 6.90 varied by 0.12 ml., thus indicating that the effect of electrolyte concentration variations is negligible under ordinary conditions.

Blank. Inherent in the proposed method was the possibility of a blank arising from residual acid in the resin and in the polyalcohol reagent. The modified titration procedure eliminated

the blank arising from the first source, and any blank arising from the polyalcohol reagent was removed by preliminary neutralization of the invert sugar solution to the equivalence point pH. Thus the blank was completely eliminated except for any boron which could conceivably be introduced from glassware or as a contaminant in reagents. The blank was experimentally shown to be nil.

Resin Rinse Requirements. The amount of water required to remove all boric acid from the resin bed was ascertained by passing boric acid solutions through the column, washing with varying amounts of water, and titrating the total effluent. Quantitative recovery of 3.08 mg. of boron in 50 ml. of solution was effected by washing the resin with 150 ml. of water in small portions (ca. 25 ml. each). In order to provide a safety factor, 200 ml. were chosen as the volume of rinse solution.

Polyalcohol. From the many polyalcohols which have been suggested for increasing the apparent ionization of boric acid, invert sugar solution was chosen because of its relative effectiveness, availability, low cost, and freedom from a reagent blank correction.

Table I. Effect of Various Ions on Determination of Boron

Sample Composition[a]	Mg.	No. of Detns.	Av. Error, Mg.	Maximum Error, Mg.	Relative Standard Deviation, %
Fe	205	4	0.00	+0.03	0.6
Al, Be, Mg, Zn	31 each	5	0.00	±0.01	0.3
Cd, Co, Cu, Hg, Ni	31 each	6	−0.02	−0.05	0.8
Th, Sn, Ti, U, Zr	31 each	6	0.00	±0.03	0.7
$Cr_2O_7^{--}$, MnO_4^-, VO_4^{---}	62 each	4	−0.01	−0.02	0.3
P	0.9	5	+0.03	+0.04	0.4
As	0.3				
Mo	0.3				
P	1.7	5	+0.07	+0.09	0.4
As	0.5				
Mo	0.5				
Si	25	6	+0.03	+0.06	1.5
Si	50	2	+0.03	+0.04	1.3
Si	200	2	+0.03	+0.04	1.3

[a] Each sample contained 3.08 mg. of boron.

Separation of Boric Acid from Cations. The efficacy of the ion exchange method for isolating boron from various interfering cations was tested by analyzing solutions of known composition. Considering the studies that had already been made of exchange of inorganic cations, it was considered sufficient to pick representative groups of ions for investigation without attempting to investigate all possibilities. The separation of boron from various ions which are known to interfere in the titrimetric determination and those which are most likely to be found in metallurgical materials was accomplished as indicated by the data of Table I. In general, the solutions were prepared by dissolving boric acid and the designated salts in 50 ml. of water containing the minimum amount of hydrochloric acid necessary to prevent hydrolysis. The described procedure proved capable of separating boric acid from at least 60 times its weight of iron and 10 times its weight of aluminum, beryllium, magnesium, zinc, cadmium, cobalt, copper(II), mercury(II), nickel, thorium, tin(IV), titanium, uranium, and zirconium. These values were experimentally verified, but do not necessarily represent the upper limit of concentration that may be tolerated. In fact, it is probable that considerably higher amounts of these cations can be quantitatively separated from boron if sufficient resin is used.

Interference of Anions. Many boron-containing materials consist largely of elements which form cations when the samples are dissolved, yet small amounts of anion-forming elements are often present. Anions containing elements that can be reduced to a valence state in which they exist as cations may then be removed by the cation exchanger.

Boric acid was separated from chromate, vanadate, and permanganate by adding 3% hydrogen peroxide to the hot 0.7 *N* hydrochloric acid solution of the sample until the samples became yellow. After the samples had boiled for 5 minutes in a flask fitted with a reflux condenser, stannous chloride was added until no further color change took place and then 5 drops were added in excess. The cooled solutions were analyzed by the usual procedure, with the results shown in Table I.

Other anions such as arsenate, phosphate, molybdate, and silicate cannot be separated from boron in the foregoing manner. Small amounts of these substances can be tolerated when the described modified titration procedure is used. The effect of these anions was to reduce the slope of the titration curves because of their buffering action and thus to decrease the accuracy of the determination when appreciable amounts were present. The data of Table I indicate that boron may be determined in solutions containing less than 0.9 mg. of phosphorus, 0.3 mg. of arsenic, and 0.3 mg. of molybdenum with a relative error of approximately 1%. As arsenic and phosphorus in steel seldom exceed 0.03 and 0.1%, respectively, a 1-gram sample could be used for the determination of boron without requiring the removal of these elements. The effect of 200 mg. of silicon was approximately in the same order of magnitude.

DETERMINATION IN COMMERCIAL MATERIALS

As no satisfactory standard boron-containing materials were immediately available, synthetic samples were made to simulate typical sample compositions.

The synthetic steel samples were prepared by dissolving appropriate sized samples of National Bureau of Standards Bessemer steel 8e in 15 to 20 ml. of 1 to 1 hydrochloric acid after adding measured volumes of standard boric acid solution. A 1.5-gram sample was used for mixtures containing less than 0.25% boron and a 1.0-gram sample was used when the boron content exceeded that amount. The sample was dissolved by heating in a flask that had been fitted with a reflux condenser. After the sample had dissolved, 1 ml. of 30% hydrogen peroxide was added to oxidize carbides and the solution was boiled 15 minutes. The samples were cooled, diluted to 75 ml., and analyzed using the described procedure.

The other samples were prepared by dissolving suitable salts in water containing the minimum amount of hydrochloric acid to prevent hydrolysis, when necessary.

The procedure was applied to the analysis of synthetic standards simulating steel, ferroboron, a casting alloy, and nickel plating solutions with the boron content ranging from 0.025 to 20% (Table II). The average relative error for determination of amounts of boron exceeding 2 mg. was −0.03% and the maximum

Table II. Analysis of Commercial Materials

Sample Composition	No. of Detns.	Av. Absolute Error, %	Maximum Absolute Error, %	Relative Standard Deviation, %
Steel				
N.B.S. steel 8e +0.025% B	4	+0.001	+0.003	8.3
N.B.S. steel 8e +0.410% B	4	+0.002	+0.003	0.5
Ferroboron				
Fe 88%, Al 4%, Si 2.5%, B 4.93%	4	−0.01	−0.02	0.2
Fe 73.6%, Al 3.1%, Si 3.1%, B 20.26%	4	+0.06	+0.11	0.2
Casting alloy				
A. Cr 20%, Co 40%, Ni 39%, B 1.03%	4	−0.01	−0.01	0.6
B. Cr 20%, Co 60%, Ni 9.8%, Mn 1.0%, Si 1%, B 7.93%	4	+0.01	+0.04	0.3
Nickel plating baths, mg.				
A. $NiSO_4.7H_2O$ 188, NaCl 37.5, $(NH_4)_2SO_4$ 95, H_3BO_3 16.89	4	−0.03	−0.08	0.2
B. $NiSO_4.7H_2O$ 450, $MgSO_4$ 66, NaCl 18, H_3BO_3 28.26	3	−0.02	−0.04	0.1

relative error was 1.0%. The standard deviation of a single value was 3 parts per thousand.

Advantages. The proposed method of analysis possesses the following advantages over currently available procedures applicable to the same concentration range: freedom from coprecipitation or occlusion of boric acid; freedom from a blank correction; no requirement of boron-free glassware, because only acid solutions are boiled and then only for a few minutes; minimum opportunity for loss of boron by volatilization because lengthy evaporation is not necessary; simple equipment; and increased rapidity and good accuracy.

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Automatically Increasing Solvent Polarity in Chromatography

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The determination of organic acids separated on silica gel columns is limited in sensitivity by the reduced resolution experienced for the more water-soluble acids. Although the literature contains procedures for improving resolution by manipulation of the solvent, the changes in polarity which accomplish this end are abrupt and are obtained by frequent manual operations. The widespread use of mechanical apparatus for the collection of chromatographic fractions necessitates a procedure that requires no attention once the separation has begun. A simple device permits the delivery of a solvent automatically but gradually increasing in polarity. Recovery studies indicate that, with the exception of oxalacetic acid the method is suitable for the quantitative determination of organic acids.

IN SEPARATIONS employing partition chromatography for organic acids, the resolving power of silica gel systems decreases with increasing water solubility of the solutes (*2*, *4*, *5*). Isherwood (*2*) proposed the use of several solvents, but was aware that no one, or even two, would suitably resolve an organic acid mixture of the complexity used in his study. In a procedure for the determination of furmaric acid (*4*), this was again recognized

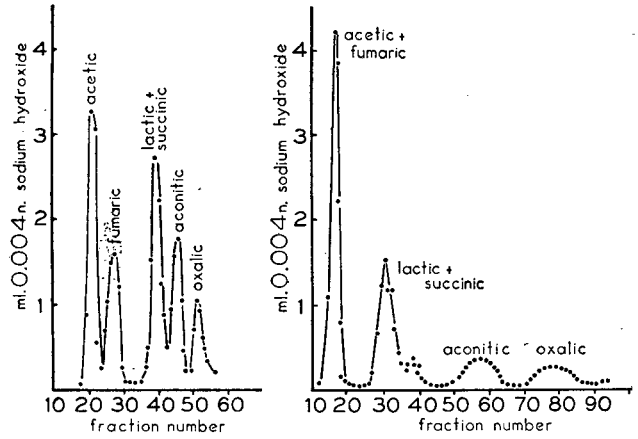

Figure 1. Chromatograms

Typical curve (*left*) resulting when chromatographic solvent progressively increases in *n*-butyl alcohol content. Typical results (*right*), when a solvent of fixed composition (10% *n*-butyl alcohol in chloroform, v/v) is employed. The difference between the character of the curves as well as the resolving power of the two systems with respect to fumaric and acetic acids contrasts here the two types of chromatographic influent. Fraction number × 2 equals ml. of effluent.

and effluent fractions on the chromatogram were collected by geometrically increasing volumes. In effect, such a procedure gradually increased the volume of polar mobile phase in each effluent fraction. Marvel and Rands (*5*) successfully employed a series of solvents progressively increasing in composition with respect to *n*-butyl alcohol. Their solvents were added manually to the column in order of increasing *n*-butyl alcohol concentration. This procedure, like the first, required constant attention and was, therefore, more noticeably disadvantageous when mechanical apparatus was employed for the collection of effluent fractions. The above procedures reduced the number of effluent fractions required to collect a given acid by manually but not gradually increasing the polarity of the mobile phase. When the concentration of each fraction was plotted against its number, the curves on the chromatogram were sharper than those obtained with a solvent of fixed polarity.

The present report, combining the principles underlying the determination of fumaric acid and those of Marvel and Rands, describes a procedure for gradually and automatically increasing the alcohol concentration and thereby the polarity of the solvent entering the column. With this method no false chromatographic peaks or shoulders on the peaks occur, as they sometimes do when the solvent polarity is increased in discrete steps. The applicability of this approach for the separation of certain acids of physiological interest is examined. A typical chromatogram employing the new procedure appears in Figure 1 (left).

APPARATUS

A device was arranged so that the stem of the solvent reservoir (*A*, Figure 2) extended to within 3 cm. of the bottom of the mixing vessel, *B*. When *A* was filled with 50% (v./v.) *n*-butyl alcohol–chloroform and *B* with 175 ml. of pure chloroform, the solvent flowing from column *C* created a fall in pressure within the system which was relieved by solvent delivered by the side arm. The 50% mixture from *A* flowed into *B* and because of the difference between the density of *n*-butyl alcohol (0.804 gram per ml.) and chloroform (1.497 gram per ml.) mixing was obtained, as demonstrated below, by the time the solvent entered *C*. As a result, the solution entering the column gradually increased with respect to alcohol concentration. *n*-Amyl alcohol (density, 0.810 gram per ml.), where indicated below, was substituted for *n*-butyl alcohol.

Table I. Observed Densities and Calculated Composition of Effluent Fractions

For a blank analysis to determine rate of mixing of two components of chromatographic solvent)

Fraction[a]	*n*-Butyl Alcohol–Chloroform Density 23°	*n*-Butyl Alcohol–Chloroform % composition *n*-butyl alcohol	*n*-Amyl Alcohol–Chloroform Density 23°	*n*-Amyl Alcohol–Chloroform % composition *n*-amyl alcohol
1	1.475	0.00	1.475	0.00
2	1.470	0.00	1.467	0.00
3	1.469	1.00	1.470	1.00
4	1.448	3.00	1.451	3.00
5	1.422	5.50	...	...
6	1.396	9.30	1.404	9.30
7	1.378	12.20	...	...
8	1.359	15.00	1.375	15.00
9	1.341	18.00	...	...
10	1.325	20.50	1.323	21.50
11	1.310	22.50	...	...
12	1.293	25.00	1.290	25.50
13	1.280	27.00	...	...
14	1.266	29.30	1.262	30.00
15	1.258	31.00	...	...
16	1.243	32.50	1.235	34.50
17	1.234	34.00	1.224	36.50
18	1.226	35.50	...	...

[a] Fraction number × 10 = volume, ml.

NATURE OF MIXING OF COMPONENTS

Solvent from the delivery apparatus was permitted to flow through a silica gel column prepared as described by Isherwood (*2*), and 10-ml. fractions of the solvent emerging from the column were collected. Densities determined at 23° are indicated in Table I. The density of *n*-butyl alcohol or *n*-amyl alcohol–chloroform is a straight-line function of the alcohol concentration. The equation for the *n*-butyl alcohol mixture is:

$$x = -151.4\,\rho + 221.8$$

where x = % *n*-butyl (v./v.) and ρ = density at 23°.

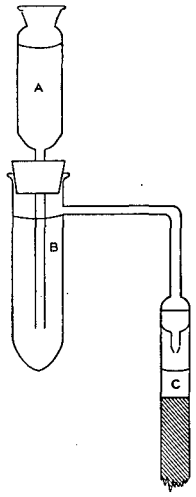

Figure 2. Dispenser for Delivering Solvent That Increases Automatically in Polarity

At start of chromatogram *A* contains 50% chloroform–*n*-butyl alcohol, *B*, pure chloroform, and *C*, progressively changing mixture from side arm. Union of side arm and column above *C* was by ground-glass joint, but can be by one-hole stopper.

APPLICABILITY FOR CHROMATOGRAPHIC SEPARATION OF CERTAIN ORGANIC ACIDS

Except for the progressively changing influent, the chromatographic analyses were like those previously described (*4*, *5*). Three-gram columns were used with a .2 ml. 0.05 *N* sulfuric acid aqueous phase. The columns had a diameter of 10 mm. and a height of approximately 30 cm. Effluent fraction volume was 2 ml. The concentration of acid in each fraction was measured by titration with standard alkali using thymol blue as the indicator.

The positions on the chromatogram and the degree to which these were reproducible are indicated in Table II. The location of all acids on the chromatogram for the mixtures was supported by evidence beyond that supplied by the repeated appearance of the acids in their first observed chromatographic positions. Effluent fumaric and aconitic acids showed, respectively, molar extinction coefficients at 230 mm. of 3.9×10^3 and 6.1×10^3 as compared with 4.1×10^3 and 6.3×10^3 of the reagent acids. The 2,4-dinitrophenylhydrazones of oxalacetic and α-ketoglutaric acids showed extinction values (*3*) identical to those for these derivatives of the reagent acids. Acetate, oxalate, and lactate were identified by known chemical procedures. Effluent succinate was mixed with an equal quantity of reagent succinate and rechromatographed. The rechromatographed succinate appeared at a position on the chromatogram like that of the original, and recovery of the total succinate admitted to the column, expressed as per cent, was 101. Recovery studies from the organic acid mixtures (Table III) indicate that, with the exception of oxalacetic acid, the method is suitable for the quantitative determination of the acids employed. No other acids were used in the study, and the purity of the acids employed was greater than 94% in every case.

DISCUSSION

The suitability of the dispensing device as an aid in controlling resolution by the chromatographic system was tested by changing from one polar solvent to another. *n*-Amyl alcohol, employed in vessel *A*, permitted (Figure 3) the separation of two hitherto unresolvable acids (*1*) by this change in the nature of the polar solvent in this procedure.

The difference between the character of the two curves (Figure 1) illustrates that the total volume of solvent required for the release of the acids from the column is decreased when the influent progressively increases with respect to alcohol content. As the rates of flow through the column for the influent of fixed compo-

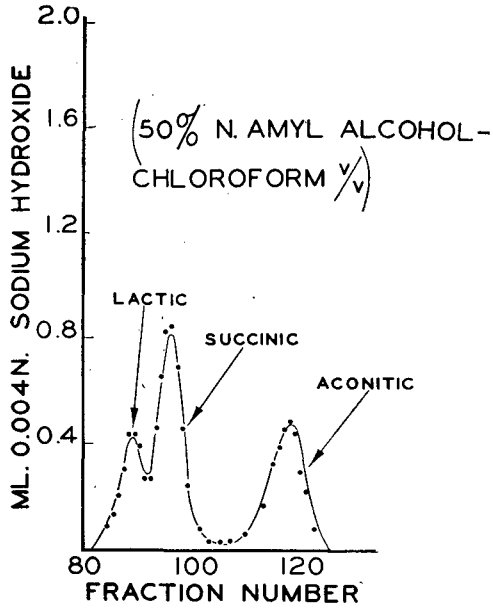

Figure 3. Chromatographic Separation of Mixture of Lactic, Succinic, and Aconitic Acids

Employing 50% *n*-amyl alcohol in vessel *A* of Figure 2
Fraction number = ml. of effluent

Table II. Observed Positions of Acids on Chromatogram

[As described by fraction of highest concentration (peak) for each acid]

Acids	No. of Chromatograms	Av. Peak Effluent[a]	Standard Deviation
Acetic	5	20.20	0.30
Aconitic	5	42.40	0.50
Fumaric	3	29.00	0.00[b]
α-Ketoglutaric	3	42.00	0.00[b]
Oxalacetic	3	47.00	1.00[b]
Oxalic	5	49.40	0.50
Succinic	6	37.00	0.00
Lactic	2	37.00	0.00

[a] Peak effluent × 2 = volume, ml.
[b] Range.

Table III. Recovery Data for Determination of Organic Acids from Mixtures

(When chromatographic solvent employed automatically increases in polarity)

Acids	No. of Chromatograms	Added, Mg., Av.	Found, Mg., Av.	Av. % Recovery	Av. Deviation
Acetic	4	1.600	1.616	101.00	0.32
Aconitic	4	0.606	0.612	100.90	0.62
Fumaric	3	2.000	2.049	102.90	0.64
α-Ketoglutaric	3	1.193	1.163	97.90	0.00
Oxalacetic	3	1.155	0.826	71.85[a]	0.00
Oxalic	4	1.154	1.536	98.84	0.04
Succinic	4	1.543	1.538	99.84	0.10
Lactic } Succinic }	2	2.100	2.100	100.00	0.00

[a] No attempt was made to account for low recoveries of oxalacetate. Decomposition probably accounted for loss.

sition and that which is changing do not differ widely, the release of the acids by the procedure described above would require a shorter time.

The observed data of Table I, where density is plotted against fraction number, would describe a curve for which the equation would be (*6*):

$$\rho = Ae^{-yb}$$

Then,

$$C = Ke^{-bt}$$

On differentiation this becomes $dC/dt = -Ke^{-bt}$ where ρ = density, A, b = constants, y = fraction number, t = time, and C = alcohol concentration (and thereby polarity).

Thus it follows that dC/dt or the change in polarity is decreasing. If the sum of the physicochemical processes accounting for the broadening of a chromatographic zone during its descent on the column were considered as a single but hypothetical event—diffusion along the longitudinal axis of the column—the change of this event with respect to time would follow from the well-known diffusion laws. Then the increase in polarity of the solvent in restricting "diffusion" is maximal when diffusion is maximal. Normal resolution by the column should be enhanced. The observed data (Figure 3) illustrate the resolution when the system described above is applied to succinic and lactic acids, a mixture previously unresolvable (*1*) on silica gel.

ACKNOWLEDGMENT

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Separation of Organic Acids from Plant Tissues

Chromatographic Technique

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Organic acids are of great significance in plant and animal metabolism. They ordinarily occur as complex mixtures, from which isolation and identification are difficult or impossible by methods currently available. Several recent papers have pointed toward the possibility of chromatographic separations. However, these have been of limited usefulness either because accurate identification was difficult or because they failed to include many important naturally occurring acids. The method reported uses an initial separation on a silica gel column followed, when necessary, by additional separations using both chromatographic and chemical techniques. It provides for separation and tentative identification of 16 biologically important organic acids. This method has been applied to the separation and identification of acids in tomato fruits and *Bryophyllum* leaves. It should have applications in metabolic studies as well as in identification of acids present in a wide variety of biological materials.

CURRENT biochemical studies have demonstrated a need for a complete and fairly rapid separation of small amounts of organic acids from biological materials. Extensive studies of the functions of organic acids as intermediates in plant metabolism are dependent upon a satisfactory method for their isolation. Most of the currently available methods for the determination of organic acids are restricted to individual acids and prove unsatisfactory when several acids are to be determined in the same sample. These methods often require treatments that destroy or alter the acids involved. Some of the limitations of existing methods have been discussed by Thimann and Bonner in a recent review (*8*).

The most satisfactory proof of the occurrence of a specific acid in plant tissues is given by its actual isolation and identification. Isherwood (*1*) has published a chromatographic method employing a silica gel column for the isolation and determination of organic acids from fruit, by which several specific acids can be separated without severe or destructive treatment. When previous knowledge of the acids present is not available, this method offers little aid in their tentative identification. Marvel and Rands (*5*) published a similar chromatographic method suitable for the separation of various organic acids but not especially well adapted to biological materials, as it fails to separate some of the commonly occurring acids. It was felt that the real potentialities of this chromatographic technique for the separation of organic acids of metabolic importance had not yet been realized.

By the use of mixtures of known organic acids, this method has been successfully extended and many separations not previously reported have been achieved. The improved technique has been applied to separation of organic acids from typical plant tissues.

APPARATUS

Nitrogen tank and needle valve
A chromatographic tube (Figure 1) 12 mm. in inside diameter, 24 cm. long, with attached stopcock
A chromatographic tube 7 mm. in inside diameter, 75 cm. long, with attached stopcock
Solvent reservoir and pressure system (Figure 1)
Intermittent siphon
Microburet, 10-ml. capacity

REAGENTS

Silica gel was prepared from Mallinckrodt's silicic acid (specially prepared for chromatographic analysis) by removal of the fine particles through repeated suspension in distilled water and decantation of the slower settling particles until approximately one third of the original material was removed. The remaining fraction containing the coarse particles was filtered, dried in an oven at 100° C. for 24 hours, and stored in a closed container.

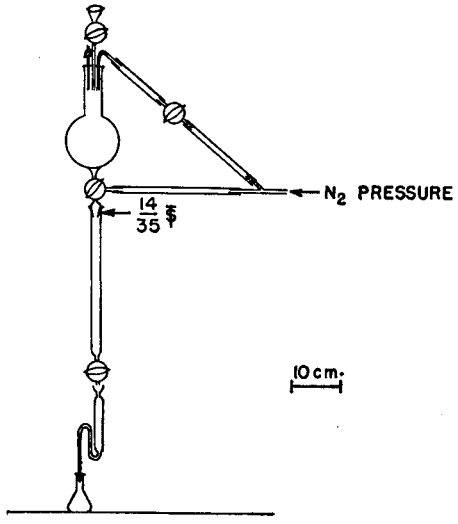

Figure 1. Apparatus

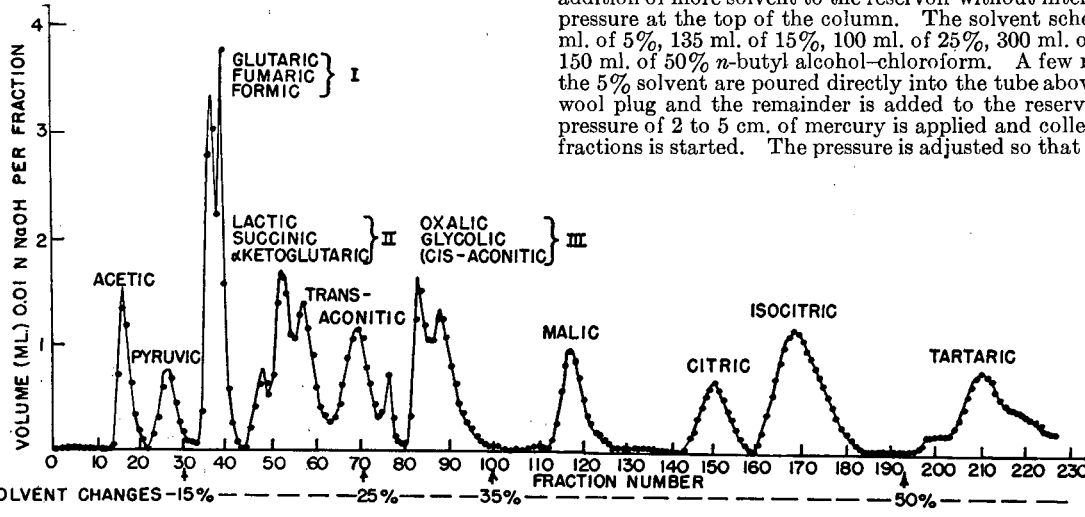

Figure 2. Results of Preliminary Separation

Eluting solvents were prepared from U.S.P. chloroform washed twice with water and C.P. *n*-butyl alcohol to contain 5, 15, 20, 25, 35, and 50% (v./v.) *n*-butyl alcohol in chloroform and from water-washed benzene and C.P. *n*-butyl alcohol to contain 25% (v./v.) *n*-butyl alcohol in benzene. Each solvent mixture was equilibrated against 0.5 *N* sulfuric acid by shaking the two phases in a separatory funnel and passing the solvent layer through dry filter paper to remove suspended water droplets.

Phenol red indicator was prepared by grinding 100 mg. of the solid with 5.7 ml. of 0.05 *N* sodium hydroxide and making up to 100 ml.

Standard 0.01 *N* sodium hydroxide (carbonate-free).

EXPERIMENTAL

The complete procedure for the isolation of the individual acid consists of a preliminary or survey separation, followed when necessary by additional separations. The survey separation is conducted by adding the mixture of organic acids to the top of a silica gel column and developing with a series of *n*-butyl alcohol–chloroform solvents. Fractions of the effluent are collected and titrated.

Procedure. The standard survey column is prepared as follows: A glass-wool plug is placed in the bottom of the chromatographic tube (12 mm. × 25 cm.) to support the column. Eight grams of the prepared silica gel are mixed with 5.5 ml. of 0.5 *N* sulfuric acid in a mortar. The resulting free-flowing powder is slurried in 60 to 70 ml. of chloroform and added to the chromatographic tube in successive portions. A gas pressure of 5 to 10 cm. of mercury is applied to the top of the tube to speed the removal of excess solvent, care being exercised not to allow the solvent level to fall below the top of the column. This procedure gives a uniformly packed column 14.5 cm. long. The mixture of free organic acids, containing a total of 10 to 100 mg., dissolved in 0.5 ml. of 0.5 *N* sulfuric acid is mixed thoroughly with 1 gram of dry silica gel and the resulting free-flowing powder is transferred quantitatively to the top of the column. This transfer is easily accomplished by pouring the mixture into the tube through a short-stemmed funnel which, along with the container, is rinsed with 2 to 3 ml. of chloroform. If the acids are liberated from their sodium salts, a slight excess of sulfuric acid may be used in the liberation with no undesirable effects. With the aid of a glass rod, the silica gel containing the sample is slurried in the chromatographic tube with the 2 to 3 ml. of chloroform used in rinsing, the excess chloroform is drained through the column, and a glass-wool plug is pressed down firmly on the surface of the sample. This plug serves to wipe down particles of silica gel adhering to the tube and also prevents disturbance of the column during addition of the eluting solvents.

Development of this survey column proceeds by addition of a series of *n*-butyl alcohol–chloroform solvents experimentally selected to give maximum separation of the metabolically important acids. These solvents are added to the top of the chromatographic column through a reservoir which permits the application of pressure from a nitrogen tank and at the same time allows the addition of more solvent to the reservoir without interrupting the pressure at the top of the column. The solvent schedule is 100 ml. of 5%, 135 ml. of 15%, 100 ml. of 25%, 300 ml. of 35%, and 150 ml. of 50% *n*-butyl alcohol–chloroform. A few milliliters of the 5% solvent are poured directly into the tube above the glass-wool plug and the remainder is added to the reservoir. A gas pressure of 2 to 5 cm. of mercury is applied and collection of the fractions is started. The pressure is adjusted so that the effluent is collected at the rate of 80 ml. per hour. Subsequent solvents are added just before the last of the preceding solvent passes into the column. The effluent passes through an intermittent siphon adjusted arbitrarily to deliver about 3.3 ml. Individual fractions are collected for titration in 25-ml. Erlenmeyer flasks, to which 8 to 10 ml. of carbon dioxide–free distilled water and 2 drops of phenol red indicator are then added, and the mixture is titrated by addition of 0.01 *N* sodium hydroxide from a microburet. Near the end point vigorous agitation is necessary to ensure intimate

contact between the two phases. The complete survey separation requires about 9 hours.

Figure 2 shows titration values obtained when a mixture of the acids indicated was chromatographed, and illustrates the relative positions of those acids completely separated by the survey procedure and the position of those separating into groups that demand further attention. The order of elution of the acids was determined by chromatographing known acids singly and in pairs.

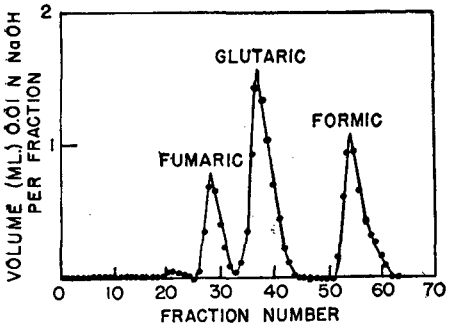

Figure 3. Separation of Group I

Fumaric, glutaric, and formic acids are not separated from each other on the survey column, but can be readily separated by a second treatment on a longer column.

The fractions containing these acids are combined in a separatory funnel and the water layer is separated. The solvent layer is washed once with water; if necessary, sufficient 0.01 *N* sodium hydroxide is added to make the solution alkaline to phenol red. The water solutions are combined and evaporated to dryness on a water bath. The sodium salts obtained are dissolved in a volume not exceeding 0.5 ml. of 0.5 *N* sulfuric acid. An amount of 4 *N* sulfuric acid equivalent to the organic acid salts present is added. This solution is mixed thoroughly with 1 gram of dry silica gel and transferred quantitatively to the top of a chromatographic column 60 cm. long and 7 mm. in diameter prepared, as described previously, from 12 grams of silica gel mixed with 8.5 ml. of 0.5 *N* sulfuric acid. This column is developed by the addition of 20% *n*-butyl alcohol–chloroform solvent. Fractions are collected at the rate of 30 ml. per hour with the aid of an intermittent siphon delivering 0.9 ml.

Figure 3 shows how fumaric, glutaric, and formic acids are separated with this longer column.

It can be seen from Figure 2 that lactic, succinic, α-ketoglutaric, and *trans*-aconitic acids are not completely separated in the preliminary separation. The degree of separation achieved does give information useful in the tentative identification of these acids. The second small peak in the *trans*-aconitic acid curve is a result of the solvent change occurring during its elution. For reasons discussed below, the separation of these acids on a longer silica gel column is not practical. If all of these acids occur together in amounts such that they are not separated from each other by the survey separation, the following procedure may be used:

The fractions containing these acids are combined and the water layer is separated. This solution of the sodium salts of the organic acids is evaporated to a volume of 10 ml. on a water bath. The α-ketoglutaric acid is separated as the 2,4-dinitrophenylhydrazone (*2*) by adding 2 ml. of a 1% solution of 2,4-dinitrophenylhydrazine in 10% sulfuric acid and allowing the mixture to stand for 30 minutes. The mixture is then extracted twice with 2 to 3 ml. of ether. The combined ether extracts are extracted once with 10 ml. of water and this water solution in turn is extracted twice with 2 to 3 ml. of ether. The combined ether layers contain the α-ketoglutaric acid derivative, and the combined water layers contain lactic, succinic, and *trans*-aconitic acid if all were initially present.

It is now possible to isolate *trans*-aconitic acid by rechromatographing this acid mixture according to the survey procedure. If both lactic and succinic acids are present, their separation is effected chromatographically by use of a modification of the method presented by Neish (*6*). The fractions which contain these acids are combined and the water layer is separated and evaporated to dryness. The free acids are liberated from their salts and added to the top of a survey column. The procedure for the preparation of the column and addition of the acids is the same as that for the survey separation. The column is developed by the addition of 25% (v./v.) *n*-butyl alcohol–benzene solvent.

Figure 4 illustrates the separation achieved by this procedure.

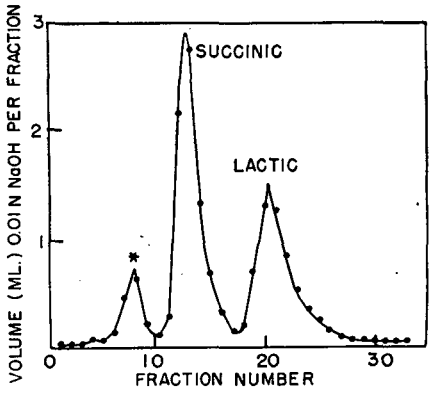

Figure 4. Separation of Succinic and Lactic Acids

*** Compound that separates whenever commercial C.P. lactic acid is chromatographed**

If the conditions of the initial extraction of the tissue are such that *cis*-aconitic acid is not converted to *trans*-aconitic acid (*8*), *cis*-aconitic acid is eluted from the survey column with glycolic and oxalic acids. The fractions containing these three acids are combined, the water layer is separated, and the solution of the sodium salts is evaporated to about 10 ml. and transferred quantitatively to a centrifuge tube. The solution is made just acid to phenol red with dilute sulfuric acid and the oxalate is precipitated by adding a slight excess of solid calcium carbonate and digesting for 30 minutes in a boiling water bath. The mixture of calcium oxalate and calcium carbonate is centrifuged, the supernatant fluid is decanted, and the precipitate is washed twice with 2 ml. of hot water. Oxalic acid may be recovered as such from this precipitate by acidification and extraction, or it may be determined by the standard permanganate titration procedure. The supernatant solution and washings are combined and evaporated to dryness, and 1 ml. of 0.5 *N* sulfuric acid is added. This acidified mixture is kept in a closed container in a water bath at 65° C. for 1 hour. This treatment quantitatively transforms *cis*-aconitic to *trans*-aconitic acid (*3*). The resulting *trans*-aconitic acid and glycolic acid are separated by addition to the top of the survey column in silica gel as previously described and elution with 20% *n*-butyl alcohol–chloroform solvent.

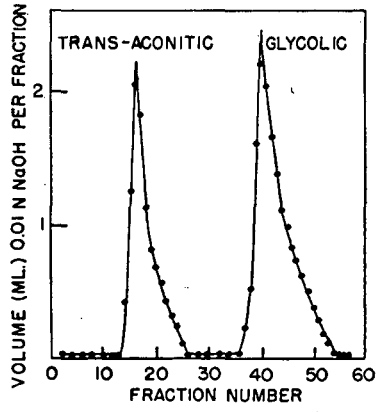

Figure 5. Separation of Group III

Figure 5 shows that separation is effected by this procedure.

Figure 2 shows that acetic, pyruvic, malic, citric, isocitric, and tartaric acids are separated completely during the survey separation.

Any of the accepted extraction methods may be adapted for use with this separation procedure. If the isolation of volatile acids is desired, Isherwood's (*1*) procedure has significant advantages. With some tissues the extraction method of Pucher *et al.* (*7*) is more convenient.

Application. Table I lists the acids found in tomato fruit and *Bryophyllum* leaves. The tomatoes were extracted by the method of Isherwood and the *Bryophyllum* leaves by the method of Pucher *et al.* after freeze-drying.

Table I. Acids of Tomato Fruit and *Bryophyllum* Leaves

Acid	Tomato Fruit	*Bryophyllum calycinum* Leaves
	Me. × 10²/10 gram fresh weight	
Acetic	2.1	2.6
Formic	0.9	..
Lactic	1.0	..
Succinic	..	1.3
trans-Aconitic	3.9	..
Oxalic	..	3.0
Malic	4.2	46
Citric	66	40
Isocitric	..	89

DISCUSSION

The reproducibility of a chromatographic procedure of this type is such that the acids present in a given tissue may be tentatively identified from knowledge of the threshold volumes of their elution. Each individual apparatus, however, should be standardized by chromatographing a mixture of several known acids before running the unknown mixture. In this way fractions of the effluent can be coordinated with each acid without the tedious task of exactly duplicating the apparatus described here.

Column Length. For a given column diameter and solvent mixture, an increase in the column length results in a directly proportionate increase in the separation of the threshold volumes of the individual acids. If the column length is increased when a series of solvent mixtures is being used, a corresponding increase in the volume of each solvent mixture is required. Attempts to adapt this relationship to the separation of those acids not separating on a short column often fail because of an increase in the volume of solvent required to elute individual acids. The "spreading" effect is most pronounced with acids having low R values—that is, a low ratio of movement of solute to movement of developing phase (*4*). For example, the separation of the acids in group II is not complete even on a 60-cm. column.

Column Diameter. For a given column length and solvent mixture, the relationship between the cross-sectional areas of the column and the amount of solvent required to elute the acids is one of direct proportionality. An increase in column diameter may be desirable when relatively large amounts of the acids are to be separated.

Solvent Composition. Changes in the *n*-butyl alcohol–chloroform ratios produce different effects on the individual acids. The order in which the acids are eluted changes with solvent composition. For example, in the 5% solvent, acetic acid immediately precedes pyruvic acid. If 10% solvent is used, the order of emergence is acetic, fumaric, pyruvic, and glutaric acid. In 20% solvent, the sequence is fumaric, acetic, glutaric, and pyruvic acid. An association effect between fumaric and formic acids was noted. These acids fail to separate in the 5% solvent but separate completely when 10% solvent is used (Figure 6). Variation in the molar ratios of formic to fumaric acids from 0.75 to 3.7 does not alter this association effect.

Degree of Hydration of Silica Gel. Within certain limits this does not seem to be a critical factor. Amounts of water varying from 30 to 70% of the weight of the dry silica gel produce minor changes in the properties of a column. As the degree of hydration of the silica gel increases, more solvent is required to elute the acids and the separation of the threshold volumes of some of the acids is increased. If 0.5 N sulfuric acid in excess of the weight of silica gel is used, excessive spreading of the acids with low R values occurs.

Preparation of Silica Gel. Removal of the finer particles from Mallinckrodt's silicic acid facilitates packing of a uniform column and reduces the pressure required to obtain a satisfactory flow rate. A column prepared from the larger particles has the same characteristics with respect to variables other than rate as a column prepared from the finer particles. Oven drying at 100° C. for 24 hours does not change the silicic acid in any way that is significant in this application.

Flow Rate. For the survey column described the rate of flow may be any rate up to 100 ml. per hour. Rates greater than this tend to produce unsymmetrical curves and spreading of acid bands. Extremely slow rates are disadvantageous because of the increased time required and the increased losses due to esterification.

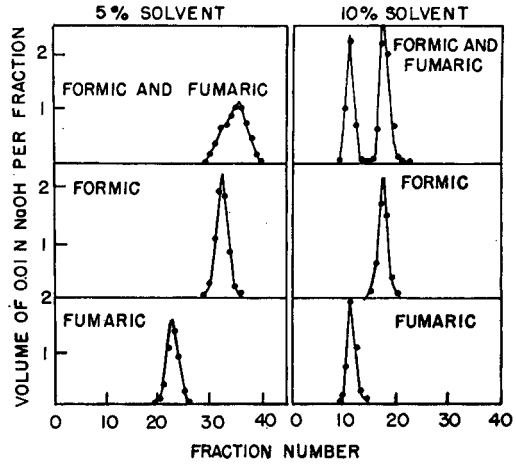

Figure 6. Association Effect

Quantitative Considerations. Recoveries of the acids vary according to the individual acid but, with the exception of formic and oxalic acids, are 95 to 100%. The recovery of formic acid after elution from the two columns is 85%; the recovery of oxalic acid is also 85%. The threshold volume of each acid is characteristic and after standardization of the apparatus may be used as a means of tentative identification. The sensitivity of the method permits detection and tentative identification of quantities as small as 2 to 10 μe. of the individual acids. If one acid is present in a relatively large amount, the presence of the acid immediately following it may be obscured. In this instance the use of a smaller sample or a column of larger diameter is recommended.

Sample Addition and Suggested Uses. The method of adding the sample to the column permits the ready addition of water-soluble acids and eliminates the difficulties encountered when a sample is introduced in a small volume of one of the solvents. The simplicity of this method of sample addition suggests its usefulness in the direct determination and separation of organic acids from such biological materials as expressed plant sap, fruit juices, milk, and certain milk products. If, as in the case of dairy products, the material has a high fat content, this can be separated from the acids by elution with chloroform before beginning the development of the column.

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A Focusing Cell Refractometer

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The focusing cell refractometer was developed as a part of a general program to improve the efficiency of the manufacture of synthetic rubbers. The refractometer has particular application to the monitoring of hydrocarbon feed streams such as butadiene and styrene and as an index of product quality. It was not possible to evaluate this instrument under actual plant conditions; however, laboratory data indicate general usefulness as a plant control medium. The accuracy of the laboratory model was ±0.0002 refractive index unit. This does not represent the maximum obtainable with this type of design. This instrument is not satisfactory for use with opaque liquids, but it is relatively insensitive to changes in sample color and to deposition of material on the cell surfaces. This latter property is of particular importance in dealing with plant streams because of the large amount of foreign material usually present. This design is especially suited to automatic temperature compensation.

A NUMBER of successful methods have been utilized for rapidly indicating or recording refractive index of liquids. The primary application of these instruments is in the control of chemical processes that may be rapidly followed in terms of refractive index changes. Instruments described have been essentially of two types: those whose operation depends on the directional change of a light beam refracted by the liquid (*1, 2, 7, 8*), and those whose operation depends on the change of intensity of light being reflected from a glass-liquid boundary (*3–5*). The latter are especially useful with opaque liquids, as the light does does not have to pass through the liquid. The instrument described in this paper is of the former type and utilizes a principle similar to that described by Melville and Watson (*6*), in which a cylindrical liquid reaction vessel was made an integral part of an optical system. This instrument is merely an experimental laboratory model and does not represent, in the performance characteristics of accuracy, sensitivity, and stability, the maximum attainable with this type of design.

THEORY OF THE INSTRUMENT

The primary element of the refractometer is a cell consisting of a glass window and a plano-convex, cylindrical lens enclosing a flowing liquid, the refractive index of which is to be measured. As shown in Figure 1, light from an incandescent source is collimated, filtered, and split into two beams that are passed through the focusing cell. At the boundary of the liquid sample and the cylindrical lens the beams will converge and intersect at a focal plane.

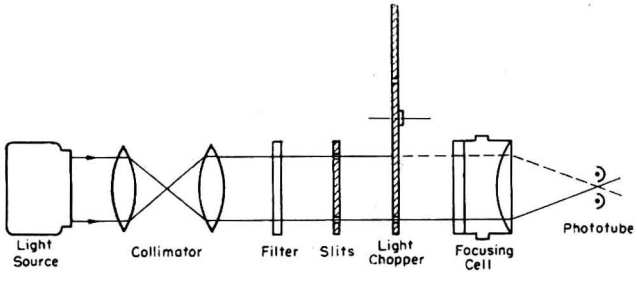

Figure 1. Optical System

The focus may be determined approximately by applying the thin lens equations of geometric optics,

$$f = \frac{r}{\eta_l - \eta_s} \tag{1}$$

where r is the radius of curvature of the lens, f the distance from the focusing cell to the focus, η_l the refractive index of the lens, and η_s the refractive index of the sample liquid.

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For any given refractometer with a cylindrical lens of fixed radius of curvature and refractive index, the position of the focal plane is a function solely of the refractive index of the sample liquid. With a suitable method of ascertaining the focus the instrument can be calibrated to indicate refractive index.

For practical design purpose the refractometer can operate through a limited focal range, specified as $f_{\text{min.}}$ to $f_{\text{max.}}$.

$$\eta_l - \eta_{s_1} = \frac{r}{f_{\text{min.}}} \tag{2}$$

and

$$\eta_l - \eta_{s_2} = \frac{r}{f_{\text{max.}}} \tag{3}$$

from which

$$r = (\eta_{s_2} \eta_{s_1}) \frac{f_{\text{min.}} \times f_{\text{max.}}}{f_{\text{max.}} - f_{\text{min.}}} \tag{4}$$

where η_{s_1} is the refractive index at the minimum focal plane and η_{s_2} is the refractive index at the maximum focal plane.

The over-all sensitivity of the focal plane position to changes in refractive index of sample is given by

$$\frac{f_{\text{max.}} - f_{\text{min.}}}{\eta_{s_2} - \eta_{s_1}} = \frac{f_{\text{min.}} \times f_{\text{max.}}}{r} \tag{5}$$

The differential sensitivity at any given focal plane within the limits of the focal range is given by

$$\frac{df}{d\eta_s} = \frac{r}{(\eta_l - \eta_s)^2} = \frac{f^2}{r} \tag{6}$$

REFRACTOMETER DESIGN

Optical System. The necessary information for the design of the cylindrical lens of a focusing refractometer may be obtained by substituting the desired sensitivity and range characteristics in Equations 1 to 6. These equations are also useful for the modification of an existing model.

The first experimental model refractometer was designed with the following data: The maximum focus, $f_{\text{max.}}$, was chosen as 120 cm. and the minimum focus, $f_{\text{min.}}$, as 60 cm. Refractive indexes of $\eta_{s_1} = 1.344$ and $\eta_{s_2} = 1.428$ were chosen to correspond to $f_{\text{min.}}$ and $f_{\text{max.}}$, respectively. Otherwise it is not clear that η_{s_1} and η_{s_2} are arbitrary.

From Equation 4 the lens radius of curvature,

$$r = (\eta_{s_2} - \eta_{s_1}) \frac{f_{\text{min.}} \times f_{\text{max.}}}{f_{\text{max.}} - f_{\text{min.}}} =$$

$$(1.428 - 1.344) \frac{(120 \times 60)}{(120 - 60)} = 10 \text{ cm.}$$

From Equation 2 the refractive index of the lens,

$$\eta_l = \frac{r}{f_{\text{min.}}} + \eta_{s_1} = \frac{10}{60} + 1.344 = 1.511$$

These two equations yield a cylindrical lens of refractive index $\eta_l = 1.511$ and radius $r = 10$ cm.

Table I. Cylindrical Lenses

	Cylindrical Lens		
	Radius of curvature	Refractive index	Refractive Index, Range
1	10	1.511	1.344 to 1.428
2	10	1.577	1.410 to 1.494
3	10	1.643	1.476 to 1.560

From Equation 5 the sensitivity is $0.72 \frac{\text{mm.}}{0.0001.}$ As even crude experimental tests indicate that the focal plane can be located to 1 mm., the over-all accuracy of the instrument is about ±0.0002 refractive index unit.

The range of the instrument can be expanded by providing a set of cylindrical lenses of appropriate design. A possible set for the experimental instrument is shown in Table I.

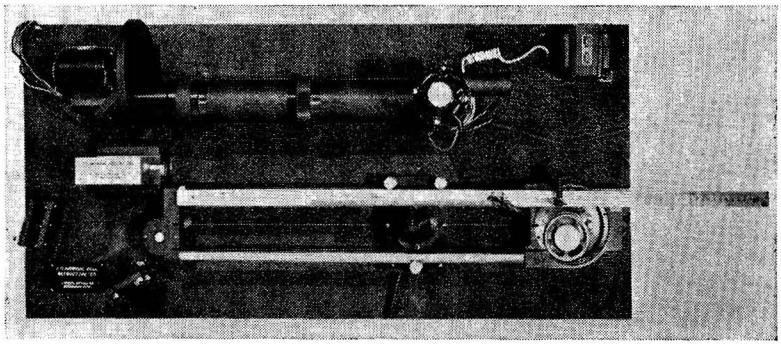

Figure 2. Focusing Cell Refractometer

Focal Plane Detection. The optical system of the refractometer is shown in Figure 1 and an instrument photograph in Figure 2. Light from a 50-watt projection lamp is collimated and made monochromatic with a red glass filter. Two slits about 0.125 inch wide and 0.25 inch high are separated by 1 inch (2.5 cm.) to form two parallel beams. The chopping mechanism consists of a synchronous motor driving a circular disk. The disk contains appropriately located axial slots which alternately intercept the two beams as the disk is rotated. It is important, at least for automatic indicating or recording, that the motor have no slippage, but lock in at exact multiples of the line frequency. For a 30-revolution-per-second motor, for example, a disk containing four slots, each 90° in length, is used to alternate the beams 60 times per second. The cell consists of a circular brass ring closed at one end by a flat glass plate and at the other end by the cylindrical lens. The cell is made just thick enough to allow suitable gasketing. Openings at the top and bottom are used for filling the cell or for pumping liquids through it.

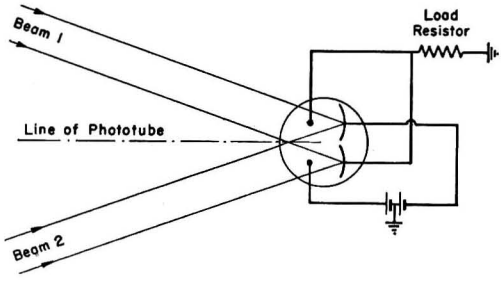

Figure 3. Principle of Phototube Operation

The location of the focus is accomplished by a dual gas phototube that can be moved along the locus of focal planes. Assume, for example, that one of the beams is blanked out, and the other beam falls on one or the other of the cathodes of the tube. Under these conditions an alternating voltage (approximately a square wave) will be developed across the load resistor (see Figure 3). If the tube is now moved in the proper direction, the beam will shift in the direction of the other cathode and an opposing signal will arise. When the voltage developed by the two cathodes is the same, the output as observed on an alternating current voltmeter will be a minimum, and the tube is considered to be located at the focal point. The use of two beams simply doubles the effect of one, thereby giving a more critical minimum. In practice it is important that each beam when used alone should result in the same focal point. This ensures that the focal point will be independent of intensity changes of either beam. Variations in the phototube sensitivity will have an effect only if the sensitivity of one cathode changes appreciably with respect to the other. An important feature of this method of detection is that it lends itself to automatic positioning of the photo tube. The signal developed, when the tube is located beyond the focal point, is 180° out of phase with the signal developed when the tube is in front of the focal point. This phase shift and the synchronization of the chopping rate and the line frequency make possible the use of a recorder amplifier and servo-motor as a null positioner for the phototube. (Amplifier and motor may be purchased separately from the Brown Instrument Co. Instructions for use with alternating current input may also be obtained from manufacturer.) The tube is mounted on a housing that is drawn along the optical path by the motor as shown in Figure 2.

Recording. The position of the phototube may be continuously recorded through the use of a balanced Wheatstone bridge circuit with a Brown Electronik recorder. A 20-ohm slide-wire is mounted along the phototube track. The slide contact is rigidly connected to the phototube housing, which is at ground potential. As brought out in Figure 4, the recorder slide-wire forms one branch of the bridge and the phototube track slide-wire the other branch. As the two slide-wires are of the same magnitude, they read ohm for ohm. Greater recorder travel per unit of phototube travel can be obtained by adding more resistance in series with the recorder slide-wire. Increasing the apparent sensitivity in this manner, however, is limited by the noise level.

PERFORMANCE

Calibration. The instrument was calibrated by circulating sugar solutions at constant temperature. The refractive indexes of the solutions are plotted against the focal plane position in Figure 5. As can be predicted from Equation 6, the sensitivity increases with increasing refractive index.

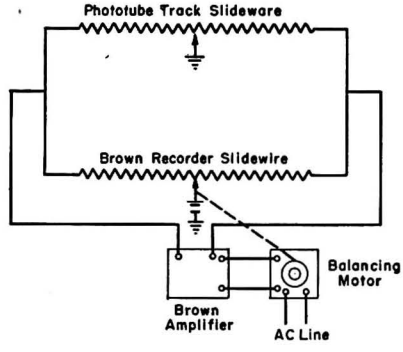

Figure 4. Circuit Diagram

Stability. Long period stability runs were made with sugar solutions circulating through the refractometer. There occurred a drift of approximately 0.0002 in refractive index per day, caused by gradual light source deterioration and imperfectly matched phototube cathodes. The stability tests indicate that standardization at least once a day is necessary in order to maintain an accuracy of ±0.0002. Standardization is accomplished by periodically circulating a standard liquid through the cell and manually shifting the phototube slide-wire until the desired reading is obtained on the recorder. This operation could be made automatic with an adequate servo-system.

Sensitivity. The noise level of the recordings of the experimental

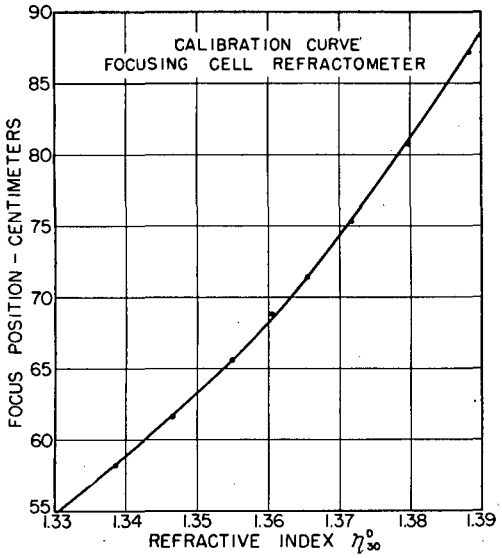

Figure 5. Calibration Curve

model is 0.0002 in refractive index. As the noise is of a constant nature, the sensitivity of the instrument is approximately 0.0001.

The sensitivity of any given instrument can be modified in somewhat the same manner as the range. Because, as indicated in Equations 5 and 6, the sensitivity is inversely proportional to the radius of curvature of the cylindrical lens, the sensitivity range is limited only by the limits of good lens design. A series of replaceable lens of equal refractive index and varying curvatures might be designed for an instrument that is to be operated through a limited refractive index range. The increase in sensitivity by this method will result in a corresponding increase in accuracy.

Temperature Compensation. Although the sample temperature was maintained to 30° ± 0.1° C. throughout the laboratory evaluation, the instrument recording bridge circuit is adaptable to standard methods of temperature compensation. A properly shunted resistance thermometer or thermistor could be used in series with the phototube track slide-wire. The problem is complicated by the nonlinear relationship between resistance and refractive index, and therefore a series of compensators would be necessary if the full range of the refractometer should be used. If the instrument should be employed as a control device to maintain constant refractive index, compensation would be straightforward.

CONCLUSION

The focusing cell refractometer provides a method for continuously recording the refractive index of transparent liquids. Limited transparent coating of the lens and predictable color changes should have no effect on operation. The experimental instrument constructed will operate with a series of three properly designed cylindrical lenses over a range of 1.34 to 1.56 with an accuracy of ±0.0002.

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RECEIVED May 4, 1951. Contribution from the Multiple fellowship on Synthetic Rubber Instrumentation of the Reconstruction Finance Corp., Office of Rubber Reserve.

Detection of Chromatographic Zones by Means of High Frequency Oscillators

P. H. MONAGHAN[1], P. B. MOSELEY, T. S. BURKHALTER[2], AND O. A. NANCE
Louisiana State University, Baton Rouge, La.

One of the obstacles to the extension of chromatography to a large number of applications lies in the difficulty of detecting the location and measuring the rate of motion of zones on the column. For this reason, the authors have adapted a heterodyne type of high frequency apparatus to the detection of chromatographic zones. Preliminary tests indicate that a wide variety of materials may be detected in this manner; the sensitivity in each case is determined by the electrical properties of the solutes, solvent, and column packing. A comparison of the measurements made with this instrument with those made by routine visual and chemical methods indicates that the results compare well within the experimental error of the customary methods. This instrument should increase the variety of compounds that may be studied by chromatography and provide a rapid and reproducible method.

THE detection of colorless zones on a chromatographic column is a difficult problem, but one in which the chromatographer is vitally interested. Various investigators have located colorless zones by extruding the column and applying appropriate streak reagents or by driving the zones completely through the column and analyzing the filtrate. Claesson (*2*) has devised a continuous, recording "filtrate analyzer," which depends upon measurements of the refractive index of the filtrate.

Jensen and Parrack (*3*) described a high radio-frequency oscillator which could be used as a chemical titrator by placing the liquid sample inside the coil of the resonant tank circuit of the oscillator and measuring the variations in plate current produced by addition of titrant. Arditti and Heitzmann (*1*) modified Jensen's method by measuring the variations in grid current. West and Burkhalter (*6*) used two matched high radio-frequency oscillators operating at the same frequency. They measured frequency differences produced by introducing samples into the tank coil of one of the oscillators; the other oscillator served as the fre

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quency reference. The frequency difference between the "working oscillator" and the "reference oscillator" could then be interpreted in terms of the nature and composition of the chemical system under investigation. Nance, Burkhalter, and Monaghan (*5*) have modified the original method, placing the liquid sample inside a small condenser (in parallel with the main tuning condenser). This change leads to a major increase in sensitivity.

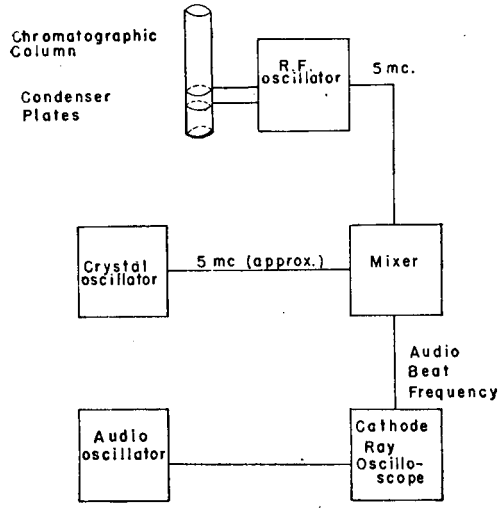

Figure 1. Block Diagram of Apparatus

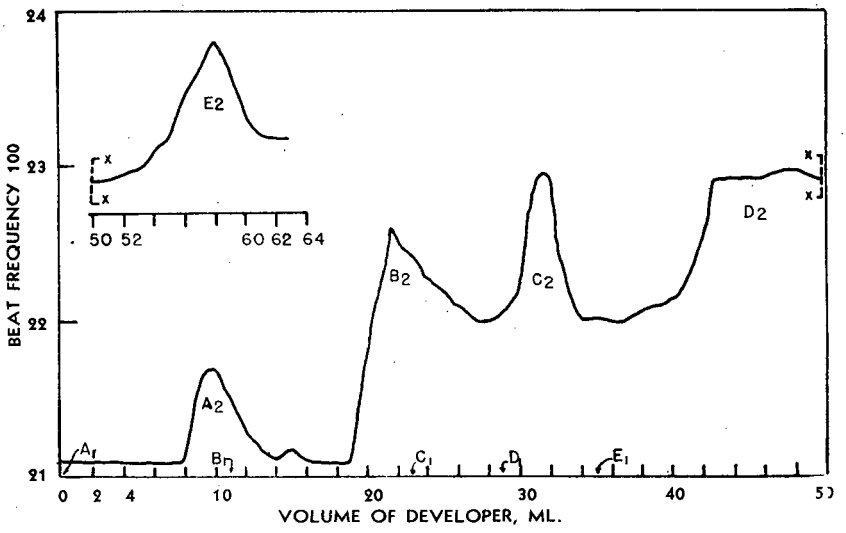

Figure 2. Several Adsorptives Run on Single Column

A. Aniline
B. Acetone
C. Phenol
D. Ethyl alcohol
E. Methanol

1. Sample put on column
2. Zone in plates

Developer, benzene

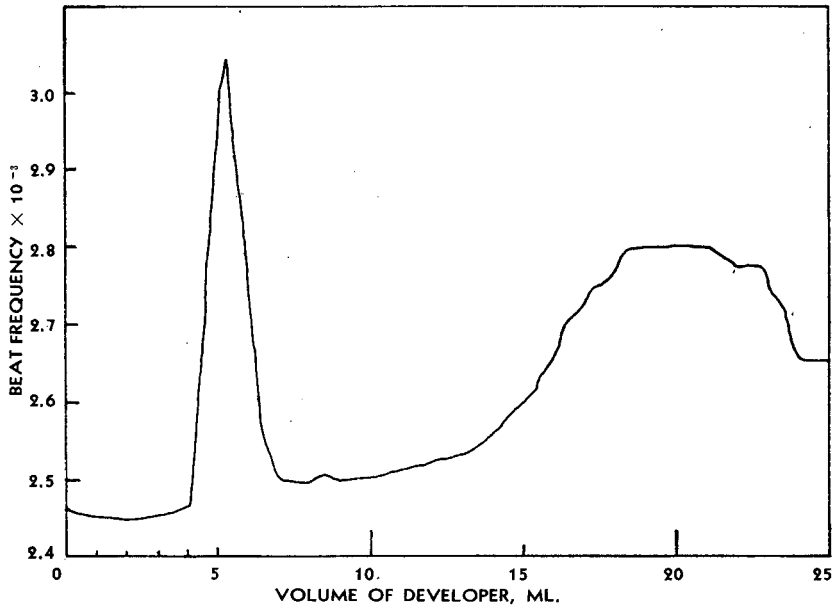

Figure 3. Separation of Nitrobenzene and Methanol

Sample volume, 1 ml.
Developer, benzene
Column length, 90 mm.

This paper describes the results obtained when a portion of the chromatographic column is placed between the plates of a capacitor in the tank circuit of a high radio-frequency oscillator.

APPARATUS

A block diagram of the apparatus used is shown in Figure 1.

The chromatographic column was made from 9-mm. borosilicate glass tubing. A small condenser was made by attaching semicircular plates of aluminum foil or copper screen, 1 cm. in length, to the walls of the column. This condenser was connected in parallel with the tank condenser of a Clapp oscillator operating in the vicinity of 5 megacycles. The output of the oscillator was mixed with the output of a crystal oscillator and the resultant audio-frequency voltage was connected to the vertical amplifier of a cathode-ray oscilloscope. A Hewlitt-Packard audio-oscillator was connected to the horizontal amplifier of the oscilloscope and the frequency difference between the radio-frequency oscillators was determined from the Lissajous figures.

The column was packed with adsorbent and, when necessary, prewashed with solvent before frequency measurements were recorded.

This method of detection has been applied to both dilute solution chromatography and displacement development. Figure 2 shows the results obtained when samples of five different compounds were run through a single column.

Table I. Comparison of *R* Value Determinations

Compound	$\dot{R}$, Oscillator	R, Streak Test
Aniline	0.74	0.76
Acetone	0.74	0.71
Phenol	0.69	0.73
Methanol	0.27	0.24
Ethyl alcohol	0.43	0.40

The adsorbent was Florisil, prewashed with 3 column volumes of benzene. The column length was 115 mm. measured from the condenser plates to the top of the packing. The samples used were 1-ml. portions of 0.5 *M* solutions of the adsorptives in benzene. The first sample was put on the column and followed by pure developer; this procedure was repeated for each successive sample. After the last sample was on the column, developer was added until all samples had passed between the capacitor

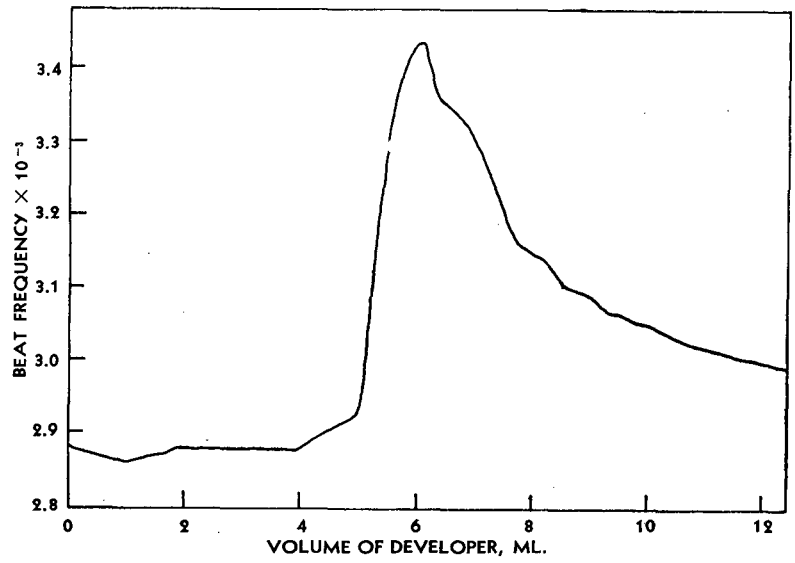

Figure 4. Incomplete Separation of Acetone and Nitrobenzene

Sample volume, 1 ml.
Developer, benzene
Column length, 107 mm.

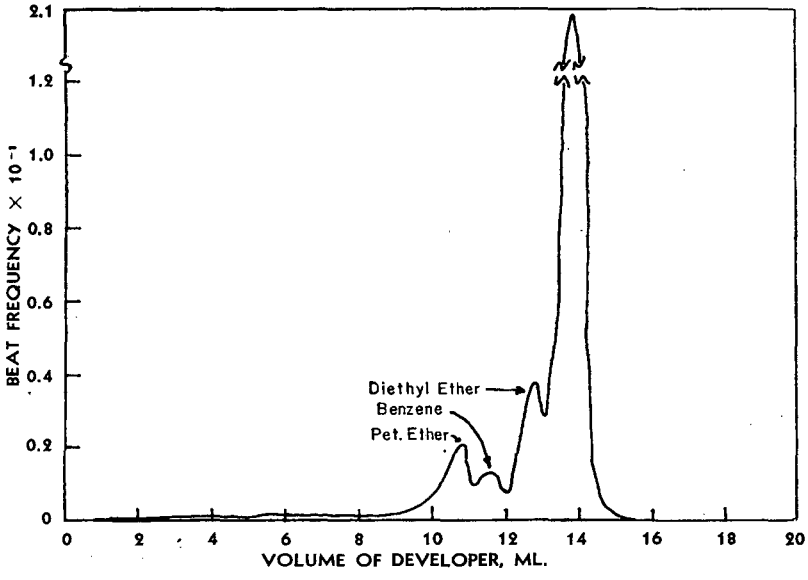

Figure 5. Displacement Development

Sample composition. 33.3% petroleum ether, 33.3% benzene, 33.3% diethyl ether
Sample volume, 3 ml. Developer, ethyl alcohol Column length, 237 mm.

plates. The working oscillator was adjusted to operate below the crystal, in order that passage of the samples through the condenser plates might produce an increase in the measured frequency difference; the effect of all materials having a dielectric constant higher than that of benzene was to lower the frequency of the working oscillator.

An inspection of the graph shows that the zones are indicated by a definite increase in the difference frequency; the difference frequency drops back to its original value very quickly after the passage of the aniline and phenol zones but compounds like acetone and methanol apparently leave a portion of the material on the column and raise the background level. This was to be expected, as previous studies by conventional methods had shown that columns washed with acetone retained, over the whole length of the column, a small amount of acetone which could not readily be washed away with benzene.

To check the validity of the zone indications given by the instrument, the R values of the compounds were calculated and checked against the R values determined by extruding the column and locating the zone by means of streak tests. The parameter, R, has been defined by LeRosen (*4*) as the ratio of the rate of movement of the leading edge of a zone to the rate of movement of the developing solvent. The agreement between the R values, as shown in Table I, is not exact but proves conclusively that the zone indicated by the oscillator is the same as that indicated by the streak test. Refinements of experimental procedures should improve the quantitative comparison of the two methods.

The separation of a mixture of nitrobenzene and methanol, in benzene solution, on a Florisil column is presented in Figure 3. The maximum at 5 ml. is due to nitrobenzene and that at 15 ml. is due to methanol. Figure 4 illustrates the effect obtained by insufficient separation of a mixture of nitrobenzene and acetone. The nitrobenzene zone starts to move out of the condenser area as the leading edge of the acetone zone moves in; the result of this phenomenon is a hump with a long trailing edge.

The procedure of displacement development involves the introduction of a mixture into the column and the use of a developer which is more strongly adsorbed than any material in the mixture. Thus, the components in the sample group themselves into zones in the order of increasing strength of adsorption and all move through the column at a rate determined by the developing solvent.

Figure 5 shows the results obtained when 3 ml. of a solution containing 33.3% each of benzene, diethyl ether, and petroleum ether B were placed on a dry Florisil column and developed with 95% ethyl alcohol. The difference between successive readings of the beat frequency was plotted against volume of solvent placed in the column and the plot of the data shows three definite peaks corresponding to the three components in the mixture. The width of each of these peaks corresponds to approximately 1 ml., a result that is consistent with the composition of the original mixture and the fact that the volume of the sample was 3 ml.

The authors believe that the sensitivity of the instrument can be improved sufficiently to permit the detection of zones of lower concentration. The time required for zone detection could be reduced by using a detached capacitor and by moving the column between its plates. Work is now directed toward effecting these improvements.

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RECEIVED June 28, 1950.

Round-Table Discussion

SILICATE ANALYSIS

Report of round-table discussion held by Division of Analytical Chemistry at 119th Meeting, ACS, Boston, Mass., April 1951

Moderator: ROBERT M. FOWLER, *Union Carbide & Carbon Research Laboratories, Inc., Niagara Falls, N. Y.*

Panel: WALLACE M. HAZEL, *Norton Co., Niagara Falls, N. Y.*
J. PAUL HIGHFILL, *New Brunswick Laboratory, Atomic Energy Commission, New Brunswick, N. J.*
R. E. STEVENS, *U. S. Geological Survey, Washington, D. C.*

IN HIS introductory remarks, Fowler stated that although silicate analysis was far too broad a subject to cover in a single afternoon, at least four phases of it would be discussed by the speakers in a way that he hoped would promote discussion.

DETERMINATION OF SILICA

In the first paper, the chairman reviewed the determination of silica. He stated that there had been few recent papers on this determination, although present methods left much to be desired, as they were long and tedious, and had many sources of error. Fortunately, the errors are both positive and negative. The methods for the determination of silica have not changed much in 50 years, the exception being the increasing use of perchloric acid, which has many advantages. As perchlorates are very soluble salts, dehydration is smoother, there is less tendency to bump, and the salts are much easier to dissolve after the dehydration. The dehydration is more rapid than with hydrochloric acid. Perchloric acid has disadvantages, too; organic matter must be destroyed, large precipitates of silica tends to decrepitate on ignition, although this can be prevented by a few washes with sulfuric acid, and finally special hoods must be used or other precautions must be taken to prevent the accumulation of residues of perchlorates and organic dusts in the hoods and duct work.

If calcium, chromium, barium, lead, and other elements that form sparingly soluble sulfates are absent, a single dehydration with sulfuric acid will usually yield more of the silica present, but sulfuric acid dehydrations tend to bump badly. Often this tendency can be reduced by the addition of oxalic acid.

With major amounts of silica, multiple dehydrations are required—at least two are standard practice. There have been a number of efforts to flocculate silica with gelatin and similar colloids. Probably the best procedure for gelatin is that of Jenkins and Webb (*2*), who dissolved the fusion in hydrochloric acid, dehydrated with sulfuric acid, took up in 10% hydrochloric acid, and added 2% gelatin. They show results that compare favorably with two dehydrations. Silica flocculated with gelatin is much cleaner and easier to wash free of other salts.

8-Quinolinol forms an addition compound with silica, but this method has never been very popular. Methods based on the formation of silicomolybdates are widely used for small amounts, but are very empirical. In some cases, they can be used with 10 to 20% of silica with fair precision. Such a method involves fusion with a carbonate-borax flux, solution of the fusion in water, careful adjustment of the pH to 1.3–1.4, addition of ammonium molybdate, then a reducing agent, usually a mixture of sodium sulfate and 1-amino-2-naphthol-4-sulfonic acid, and measurement of the absorption at 820 mμ.

A very old method, that is not widely used but has considerable value, is precipitation of the silica as K_2SiF_6, followed by titration with sodium hydroxide. This method was first described by Stolba in 1865. While it is a standard method in the sodium silicate industry, it is not usually found in standard texts, although recently German investigators have applied it to steels and cast irons with very good results. Aluminum, titanium, zirconium, and sulfuric acid interfere. The interference of aluminum is the worst, although this can be minimized by working in strong hydrofluoric acid where K_2AlF_5 is most soluble. Iron can be complexed with oxalic acid. When applicable, it is a very rapid method, as it involves only the solution of the sample, filtration, and titration of the precipitated K_2SiF_6 with standard sodium hydroxide.

DECOMPOSITION OF REFRACTORY SILICATES

Hazel discussed, first, the decomposition of refractory silicates. In his experience, the best flux for fusing these materials is a mixture of equal parts of sodium carbonate and sodium borate. This approaches a universal flux, and samples as coarse as 24-mesh can be decomposed in not over 20 minutes. The sodium borate must be specially dried to prevent frothing.

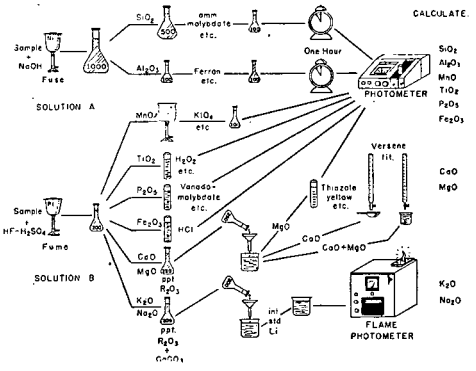

Figure 1. Flow Diagram for Rapid Analyses of Silicate Rocks

The boron may be volatilized as the methyl ester, although the speaker stated that in the laboratory they did not remove boron, yet had found no interference with it in the R_2O_3 separation. The flux is excellent for ores, as many contain fluorine which would cause losses during dehydration if borate was not present. With proper washing, the silica will not be contaminated with boron. This flux is also useful for zirconia and zirconium ores, yielding a much more readily soluble melt than either salt alone.

Another useful method for decomposing refractory materials is heating in a sealed tube with hydrochloric acid (*3*). Fused alumina, alumina refractories, beryllium oxide, and many ores and minerals can be decomposed by this treatment. The procedure is very convenient for special analyses such as nitrogen in refractory nitrides or the state of oxidation of oxides, as the decomposition can be effected in an inert atmosphere.

Spectrographic methods have considerable utility in refractory analysis. A special source unit giving large currents is employed (*1*). The direct current arc is used for a number of determinations,

such as alkali in refractories, and iron, aluminum, calcium, and magnesium in refractories and abrasives. For most analyses, the finely ground sample is mixed with 3 to 4 parts of graphite and pressed into a pellet, which is placed in the crater of a special pedestal-type graphite electrode. This type of electrode is very useful for refractory materials because it prevents the heat from being carried away too rapidly. In general, a spectrograph does not replace chemists but does relieve the chemist of many tedious hours of work and results in a more efficient relation between the chemist and his employer.

ANALYSIS OF BERYLLIUM ORES

In his discussion of the analysis of beryllium ores, Highfill described the decomposition of the ore with sodium carbonate or sodium carbonate–sodium borate although, in general, sodium carbonate is all that is required. A ratio of 4 to 5 parts sodium carbonate to 1 of ore is satisfactory and decomposition is usually complete in 30 minutes at 900° C. The fusion is taken up in hydrochloric or perchloric acid and double dehydrations are made for silica. Perchloric acid is faster and gives much purer silica. The silica is volatilized with hydrofluoric-sulfuric acid and the residue is recovered by fusion with sodium pyrosulfate. The hydrogen sulfide group is separated, and if phosphorus is present, it is separated with ammonium molybdate. The R_2O_3 oxides are separated by a double precipitation with ammonium hydroxide at the bromcresol purple end point. Then iron, titanium, and aluminum are separated with 8-quinolinol or if aluminum is required, iron and titanium are separated with cupferron and aluminum is separated from beryllium by precipitation with an acetic acid solution of 8-quinolinol from an ammonium acetate solution. The speaker described a number of tests on this separation procedure, which showed that results for alumina tended to be high by about 6 parts in a thousand when the precipitate was dried at 130° to 140° C. and weighed as such. In a number of tests, no beryllium oxide was found in the aluminum precipitates. The beryllium oxide is determined in the filtrate by precipitation with ammonium hydroxide at the phenol red end point. It is not necessary to remove the excess 8-quinolinol. Recoveries were good and contaminants were less than 0.2 mg. of alumina and a trace of ferric oxide, but no titania or zirconia.

ANALYSIS OF GRANITE AND DIABASE

Stevens presented some results of a cooperative study of the analysis of samples of granite and diabase. After the results from some thirty laboratories were compared, the composition of these samples is still not known. Results for silica varied about 2%, while those for alumina varied about 3%. As few of the methods as written were faulty, the variation must be due to the varying skill of the analysts and the care taken by them in the lengthy procedures used.

This was one of the incentives for starting a program on rapid procedures at the survey; also, procedures had to be developed to meet a rapidly expanding geological program. The methods were designed to give reliable estimates when only estimates were needed, but the accuracy approached that of conventional methods while requiring only about a sixth of the time to perform.

The methods are shown in outline form in Figure 1. Quantitative separation of precipitates is entirely avoided, most of the measurements are made photometrically, and procedures were planned to involve a minimum of manipulation. As the chief source of error in rock analysis is in the separations, and this takes most of the time, separations were avoided as far as possible.

Each constituent is determined independently—for example, silica and alumina after fusion with sodium hydroxide in a nickel crucible and solution in hydrochloric acid–silica by the molybdenum blue reaction and alumina with ferron. In a second sample decomposed by hydrofluoric and sulfuric acid, iron, titanium, manganese, phosphorus, and magnesium are determined photometrically. Calcium and calcium plus magnesium are determined by titration with disodium dihydrogen ethylenediamine tetraacetate (Versene) and the alkalies with the flame photometer. The R_2O_3 group is removed with ammonium hydroxide–ammonium carbonate before the alkali determinations. For a rapid determination of total iron, measuring the color in hydrochloric acid is reliable even in the presence of considerable phosphate. Rapid ferrous oxide, carbon dioxide, and combined water determinations are still being sought.

Stevens showed a number of comparisons of results by conventional and rapid procedures on typical rocks. These showed that, although the rapid methods did not have the inherent accuracy of the conventional procedures, the results are sufficiently accurate to meet the usual requirements of this work and have a high degree of dependability because of the simplicity of the operations involved.

In the discussion a number of questions were raised and answered by the speakers about different phases of silicate analysis.

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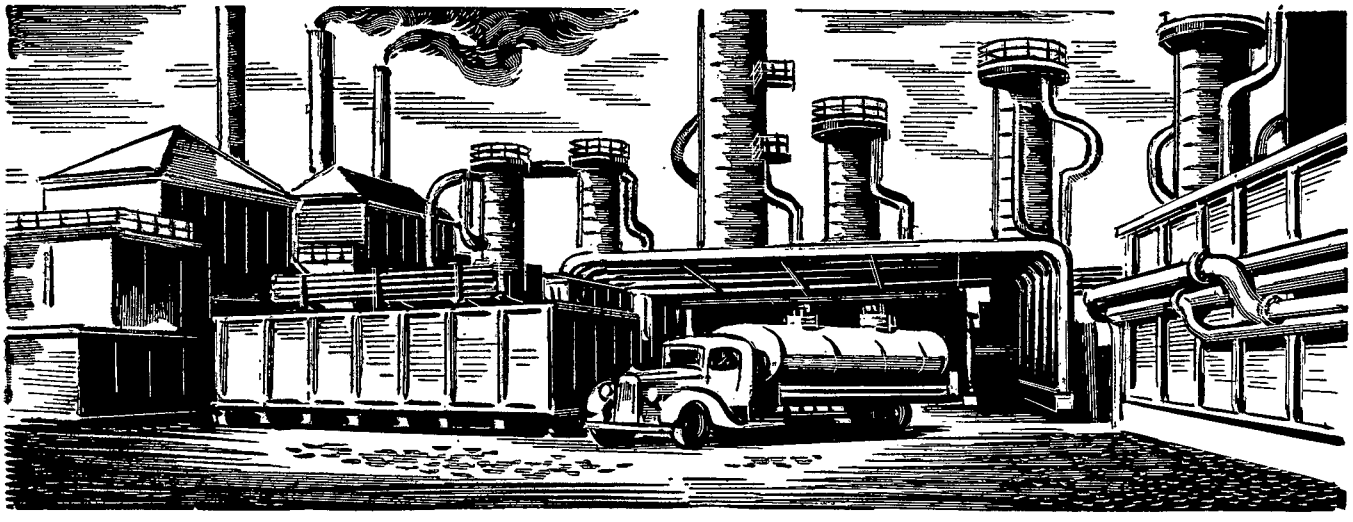
RECEIVED October 25, 1951.



Round-Table Discussion

Chemical Analysis by High Frequency Methods

Digest of round-table discussion held by Division of Analytical Chemistry at 119th Meeting, American Chemical Society, Cleveland, Ohio, April 1951

Moderator: W. J. BLAEDEL, *University of Wisconsin, Madison, Wis.*

Panel: T. S. BURKHALTER, *North Texas State College*
D. G. FLOM, *Pennsylvania State College*
GEORGE HARE, *Beckman Instruments, Inc.*
F. W. JENSEN, *Agricultural and Mechanical College of Texas*

SINCE widespread attention was called to the high frequency method of chemical analysis several years ago (*5*), it has created much interest among analytical chemists.

Briefly, the method is one for measuring solution concentrations without material contact of any sort with the solution. When placed within the coils or condensers of a high frequency oscillator, the solution affects the characteristics of that oscillator to an extent determined by the nature and concentration of the solution. These characteristics, such as plate or grid current, plate or grid voltage, or frequency, are easily measurable, and therefore any of them serve as a measure of the concentration of the solution.

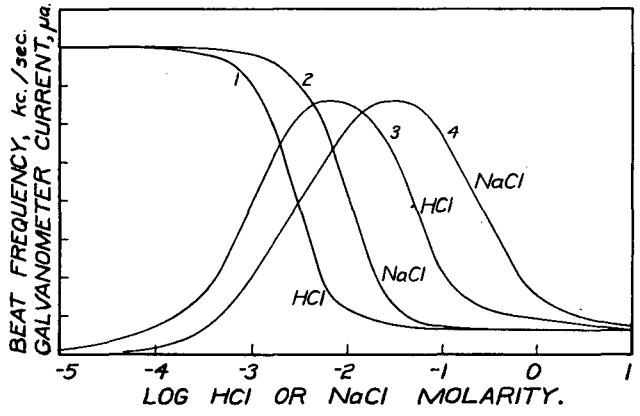


Figure 1. Response of Two Different Types of High Frequency Instruments for Solutions of Electrolytes

Till recently, attention has been centered largely upon instrumentation. There are several good instruments now available, and increasing interest is being shown in the theoretical aspects of the method and in the possible applications.

INSTRUMENTS

The instruments described in the literature are of two types, according to the nature of the response to an electrolytic solution. The current-measuring type has a response which passes through a maximum with concentration of the electrolyte (curves 3 and 4, Figure 1). The frequency-measuring type has a response which is S-shaped (curves 1 and 2, Figure 1). For both types, there are certain regions of concentration wherein the instruments are insensitive to changes of concentration, while in other regions the response varies almost linearly with concentration of the electrolyte.

The location of the maxima and points of inflection of these response curves depends almost entirely upon the operating frequency, and the regions of adequate sensitivity—i.e., those regions where response changes adequately with concentration—may be selected by selecting the frequency (*3*).

It has also been established that the solution is coupled capacitively into the oscillating circuit, and that considerably greater sensitivity results from loading a condenser-type circuit element with the solution, rather than an inductive-type element such as a coil (*1, 3*).

The frequency-measuring type of instrument lends itself very readily to a recording system. The frequency change may be converted to a direct current voltage whose magnitude is proportional to the change, and whose sign is dependent upon the direction of the change. This voltage may be recorded with a standard instrument, such as a Brown recorder. The application of this type of instrument to monitor industrial process solutions is apparent. A recording instrument might also be used in theoretical work to decrease the effort associated with measuring reaction rates (*1*).

It was stated that it would be very desirable to have an instrument that would differentiate between the resistance and capacitance of the solution, and would measure each. Work is progressing on two such instruments, but these were not described in detail (*2, 6*).

THEORY OF THE RESPONSE

The equivalent circuit of the solution shown in Figure 2 seems adequate to explain the responses of both types of instruments described above (*3*).

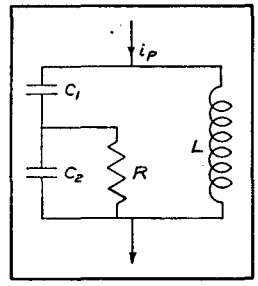


Figure 2. Equivalent Circuit of Solution

In this circuit, L represents the inductance of the network, and C_1 represents the series capacitance, which includes that through the walls of the solution container. C_2 is the capacitance of the solution itself, which is constant within a few per cent over a wide frequency range, as the dielectric constant of water is independent of frequency, except at very high frequencies. Also, C_2 is independent of electrolyte concentration. R is the resistance of the solution, inversely proportional to the conductivity and varying greatly as the solution changes from dilute to concentrated.

To explain the response of the kind in curves 3 and 4, Figure 1, it should be realized that as R is varied by changing solution concentration, the other circuit constants remaining roughly constant, the power absorption of the solution passes through a maximum, and therefore so does the plate current. At high concentrations, R is small and passes current with little absorption. Absorption increases with R until a certain limit is reached, above which C_2 begins to shunt greater portions of the current. When R is very high, energy absorption is very small because the current in R is small, and losses in R decrease as the solution is diluted.

To explain the S-shaped curves, it need only be realized that when the impedance of R becomes small compared to that of C_2, the latter is almost shorted out, and the frequency approaches $(1/2\pi)\sqrt{1/LC_1}$ in concentrated solutions. In dilute solutions, where the impedance of R is large compared to that of C_2, the

frequency approaches $(1/2\pi)\sqrt{(C_1 + C_2)/LC_1C_2}$. In the intermediate regions, where the two impedances are the same order of magnitude, the frequency varies monotonically with concentration between these two limits.

The equivalent circuit of Figure 2 explains quantitatively data obtained with both kinds of instruments. The concentration corresponding to maximum absorption may be derived as a function of frequency from the circuit of Figure 2, and the relation is the same as that obtained using Falkenhagen's equation for the relaxation time of ionic solutions.

APPLICATION TO TITRATIONS

A desirable situation exists when an unloading of the oscillator takes place during titration (*4*) due to the formation of un-ionized or insoluble substances, followed by an increase in loading caused by an excess of titrating agent beyond the end point. The choice of the titrating agent which produces an insoluble substance frequently presents problems, in that the precipitate must be quickly and quantitatively formed and must show low absorption properties.

Many oscillating circuits are not responsive to changes in heavily loading solutions, where the ion concentrations are high, as in marine waters. Modifications may be made so that the response varies linearly with concentration in these cases.

The titration of calcium with standard soap solution was discussed.

Also presented were preliminary data on the saponification of ethyl acetate to show the feasibility of following reaction rates by the high frequency method. Readings of concentration changes may be made instantaneously as reaction proceeds.

APPLICABILITY OF HIGH FREQUENCY METHODS TO ORGANIC SYSTEMS

Many organic solutions do not show the decreasing sensitivity with increasing concentration that ionic solutions do (*1*, *2*). For such nonconducting solutions, where the impedance of R is always much greater than that of C_2, examination of Figure 2 shows that the response is inherently simpler than that of conducting systems, for all changes are essentially capacitive.

If the particular instrument, temperature, and volume of solution are held constant, the frequency change upon insertion of any particular substance is a fixed property of that substance, and is measurable (*1*). This property, called the frequency change, may be handled in the course of analysis as though it were additive for ideal solutions. Ideality and a linear response are not necessary for analysis, however (*1*, *2*). By use of a working curve, it is possible to determine the water content of alcohol (*1*). The composition of *o*-xylene in *p*-xylene may be determined with an accuracy of 1% (*1*). Even ternary systems may be so analyzed. An example is water-benzene–methyl ethyl ketone. The frequency change upon removal of water by absorption in calcium chloride is dependent only upon the water content, and independent of the benzene–methyl ethyl ketone ratio. The remaining binary system is analyzed as described above (*1*).

By forming a condenser of two semicircular plates wrapped around the bottom of a chromatographic adsorption column, the high frequency method may be used to detect the passage of colorless substances down the column. Solutions of aniline, acetone, phenol, ethanol, and methanol were consecutively developed on the same Fluorosil column (*1*).

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RECEIVED October 30, 1951.

Round-Table Discussion

Determination of Nitrogen and Sulfur in Steel

Report of round-table discussion held by Division of Analytical Chemistry at 119th Meeting, American Chemical Society, Cleveland, Ohio, April 1951

Moderator: H. F. BEEGHLY, *Jones & Laughlin Steel Corp., Pittsburgh 7, Pa.*

Panel:

For Nitrogen

JOHN J. FUREY, *Union Carbide & Carbon Corp., Niagara Falls, N. Y.*
W. R. SAYRE, *United States Steel Co., Braddock, Pa.*
JOHN L. HAGUE, *National Bureau of Standards, Washington, D. C.*

For Sulfur

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INTEREST in the determination of nitrogen and sulfur in steel stems from the fact that each is unavoidably present in commercial steel and each has an important influence on the mechanical properties of the metal. Full recognition of the significance of nitrogen has come only within comparatively recent years; this has evoked an active search for reliable and economical methods for its determination, especially in the concentration range from 0.002 to 0.015% most commonly encountered in carbon steels. The determination of sulfur was one of the first required of the metallurgical chemist; it has always been one of the elements most frequently determined. With the widespread use of the spectrograph and introduction of more severe performance requirements for steel has come the need for more effective and rapid sulfur procedures—a need that has not yet been fully satisfied.

The purpose of this round-table discussion was to consider applied methods for determining nitrogen and sulfur in steel. While it was not possible to cover all procedures, typical methods

in regular use for each element were described. Then, time was allotted for an informal question and answer period with discussion of methods for each element. The applied rather than the theoretical aspects were emphasized, with an attempt to focus attention on steps where practice has not yet caught up with theory.

DETERMINATION OF NITROGEN

The determination of nitrogen in steel may be traced to a paper by Baker and Stuart (*3*) entitled "On the Existence of Nitrogen in Steel" given before the Chemical Society in London in 1864, the moderator stated, opening the discussion. A quotation from this paper reads: "Experiments were made with the intention of throwing some further light on the vexed question, 'Is nitrogen an essential constituent of steel?' and if so, whether its presence in greater or less quantity could be held to be accountable for the difference in quality of various kinds of steels." They passed purified hydrogen "more or less dried" over the steel heated to a full red heat and absorbed the ammonia formed by its reaction with nitrogen. Baker and Stuart reported values ranging from 0.007 to 0.011% for Bessemer steel but obtained values varying from 0.000 to 0.068% on identical samples.

Their conclusion stated in part "and from the whole we give it as our opinion that nitrogen is not an essential constituent of steel or iron, that it rarely exists in them even as an accidental constituent and that it has nothing whatever to do with the respective qualities of different samples of these substances... Without wishing to undervalue the research of others, we may express a doubt whether the nitrogen they obtained was not altogether derived from those sources"—i.e., from atmospheric nitrogen and impure hydrogen.

The work of Baker and Stuart appears to have been accepted in their day; at least it was not challenged publicly until 15 years later, when Allen, also a fellow of the Chemical Society, gave a paper on "Preliminary Experiments to Determine the Existence of Nitrogen in Steel" (*1*) before the Iron and Steel Institute. Allen described two methods for determining nitrogen, both of which he said avoided the shortcomings of methods used by others. The first utilized the reaction of steam with steel turnings at a red heat to decompose the water and make hydrogen and iron oxide. The nitrogen in the iron reacted with this hydrogen to form ammonia. Allen absorbed this ammonia and precipitated it as yellow ammonium chloroplatinate. This was considered conclusive proof that nitrogen was present in the steel. In his second method, Allen dissolved the sample in hydrochloric acid, distilled the solution with alkali, and determined the ammonia in the distillate by Nessler's method.

This extremely delicate test for ammonia was unknown at the time Baker and Stuart did their work. Allen thus had a new tool at his disposal. He obtained concordant results on repeated analyses of the same sample and found amounts ranging from 0.005 to 0.015% on different samples of steel. He concluded that these amounts would have been disregarded if obtained by methods previously used. Allen said in ending his paper: "Owing to the difficulty of detecting nitrogen, metallurgists have been in the habit of ignoring its possible existence in iron and steel; but now that it can be readily sought for and determined, doubtless more attention will be paid to it." The meeting was thrown open to a discussion of Allen's preliminary findings. Lowthian Bell commented ".... it must not be omitted from this consideration that the quantities dealt with were of a very trifling amount—0.005% is so small, indeed, that the mind can scarcely realize it. It had been pointed out (Bell stated) when Allen brought the same subject before the British Association meeting, that there was a great difficulty, in employing any vessel, to be sure that it was free from atmospheric air; and he (Bell) would now say that it was not proved altogether to his satisfaction that air had been entirely absent...."

E. Riley commented ".... that unless they were exceedingly careful when dealing with infinitesimal quantities of nitrogen, they hardly liked to draw the conclusion that the nitrogen might not come from the air...."

At the end of the discussion, Allen was said to have made a few observations. These are unrecorded, and one wonders what he said in reply to his critics, but he was back the next year to give a paper entitled "Further Experiments on the Existence of Nitrogen in Iron and Steel" (*2*) which he introduced by saying, "while the experiments about to be described prove the presence of small proportions of nitrogen in commercial iron and steel beyond the possibility of further doubt or cavil, I have made no attempt to ascertain the condition in which the nitrogen is present." He went on to describe the tests he made to prove that nitrogen was present in steel and not present in hydrogen-reduced iron.

The chemistry of the procedure recommended by Allen in 1880 is the same as that used today, although there have been many modifications and refinements in both the apparatus and procedure. A majority of all the published values for nitrogen in steel has been obtained with the Allen method.

The only method other than Allen's that has been investigated extensively is the vacuum fusion procedure, worked out primarily for the determination of oxygen in steel, and first used in this country by Jordan and Eckman (*7*) at the National Bureau of Standards.

This, very briefly, is the history of work on analytical methods for determining nitrogen in steel. The procedure consists of three essential steps: (1) decomposition of the specimen and of the nitrogen compounds in the steel; (2) evolution of nitrogen from the sample; and (3) measurement of the evolved nitrogen. Steps 1 and 2 are carried out simultaneously in the vacuum fusion method when the specimen is melted in a graphite crucible in vacuum at a high temperature.

Nitrogen Panel. Members of the nitrogen panel then described methods in current use in their laboratories.

Furey said that of the nitrogen determinations made at the Niagara Falls Works, those involving low carbon ferrochrome far outnumber all others. For regular grades of ferrochrome where the nitrogen content is under 0.10% the method used is as follows:

A 5-gram sample is transferred to a 500-ml. Kjeldahl flask, 60 ml. of hydrochloric acid (1 to 1) are added, and the solution reaction is allowed to proceed at room temperature for approximately 10 minutes until the rate of reaction slows down. The flask is then immersed in boiling water and heated until solution of the sample is complete. This will require approximately 20 minutes if material sized to pass a 40-mesh sieve is used.

The flask and contents are cooled to room temperature and 40 ml. of citric acid (50% solution in water) are added together with a few pieces of pumice to minimize bumping during distillation (tartaric may be used in place of citric acid). Then 300 ml. of water are added, the solutions are mixed, 60 ml. of sodium hydroxide are added (50% solution in water), and the apparatus is assembled immediately. The delivery tube from the condenser is immersed in an absorbing solution prepared by diluting 20 ml. of 0.0357 *N* sulfuric acid with 200 ml. of water contained in a 500-ml. receiving flask. Two drops of sodium alizarin sulfonate indicator are added.

Heat is applied directly to the Kjeldahl flask and distillation started. Approximately 150 ml. of distillate containing all the nitrogen originally in the specimen are evolved in 30 minutes. At the end of the distillation, the excess sulfuric acid in the receiving flask is titrated with 0.0357 *N* sodium hydroxide.

For materials such as nitrogen-bearing ferrochrome, which contains up to 0.75% nitrogen, a 2-gram sample is used.

A blank determination is run with every set of samples and is generally found to be consistent. An occasional lot of sodium hydroxide has been found which gives the normal low blank but which, when used, gives high nitrogen values. When treated with Devarda's alloy, and then heated, ammonia is evolved. Similar results have been obtained when sodium nitrate is added to purified sodium hydroxide, indicating that an occasional lot contains nitrates as an impurity. In the presence of ferrous iron, sufficient nitrate is reduced during distillation to give a high nitrogen value. When blanks are run in the absence of a reducing agent, the normal low blanks are obtained. As a precaution, it is always advisable to use for the blank determination a specimen of

known nitrogen content rather than all the reagents with the specimen omitted. All apparatus must be flushed free from ammonia by distillation of water which contains sodium hydroxide.

Citric or tartaric acid is used to hold most of the iron and chromium in solution and facilitate distillation. It also helps avoid caustic entrainment, which results if the boiling becomes too violent during distillation.

The foregoing procedure is applicable to carbon steels and alloys such as ferrochrome which dissolve readily without leaving a residue containing nitrogen. Many alloys, especially the more complex ones, as, for example, Stellites and some columbium-bearing alloys, require a different solution procedure.

In such cases, a 5-gram sample is allowed to react in a 250-ml. beaker with 50 ml. of hydrochloric acid (1 to 1) containing 2 to 3 ml. of hydrofluoric acid. When the reaction is completed, 50 ml. of a 4% solution of boric acid are added and the mixture is filtered. The residue is washed with dilute hydrochloric acid and the nitrogen determined in the filtrate plus washings by the same procedure as for carbon steels. The value so obtained is the soluble nitrogen.

The filter paper and residue are transferred to a 500-ml. Kjeldahl flask, 200 mg. of powdered copper and 25 ml. of sulfuric acid are added, and the residue is digested until the carbon is gone. Then the mixture is cooled, a few crystals of potassium permanganate are added, the solution diluted, and the digestion is repeated. Ammonia is then distilled from this solution by the same procedure as for carbon steels. The value so obtained is the insoluble nitrogen. In many alloys, the proportion of nitrogen combined in the insoluble form is too high to be neglected.

The Edgar Thompson Works of the United States Steel Co. makes carbon steel with a nitrogen content in the range of approximately 0.006 to 0.012%, Sayre stated. For determining nitrogen in this steel, very simple apparatus, dissolving, distilling, and titrating techniques are used.

The analyses are made in a basement room isolated from general laboratory work. A 5-gram sample is transferred into an 800-ml. Kjeldahl flask and dissolved in a sulfuric-phosphoric acid mixture (prepared by adding 300 ml. of sulfuric acid and 90 ml. of phosphoric acid to 1 liter of ammonia-free water). Following this simple treatment, the solution of the sample is ready for transfer to the distilling apparatus. The still consists of another 800-ml. Kjeldahl flask provided with a special distilling head so designed that all solutions can be added to the flask without opening it to the air. There is, therefore, no danger of losing nitrogen in the process of assembling the apparatus and mixing the acid solution with the caustic. The distilling flask is preceded by a 1-liter steam generating flask and followed by an Allihn condenser. Rubber stoppers are used for connections with a modified Volhard receiving flask attached to the condenser. This flask is so designed that a liquid seal always prevents escape of the ammonia.

Before starting any series of distillations, the complete apparatus is steamed out thoroughly. The receiving flask containing 10 ml. of 0.4% boric acid solution, to which have been added 2 to 3 drops of mixed indicator and just enough 0.00714 *N* acid (1 or 2 drops) to produce a faint pink color, is then put into place. The distilling flask is charged with enough sodium hydroxide solution (33%) to provide an excess of approximately 20 ml. The flask is then clamped in place. If preferred, the flask may be put in place empty and the caustic charged through the funnel top. In either case, the caustic solution is followed by the solution of the sample and then by enough water to make the volume 400 ml. Adherence to this order of additions is essential. Heat is applied at once by 550-watt heaters to both the steam generating and distilling flasks. Delivery of distillate begins in from 1 to 3 minutes and the distillation is complete about 10 to 12 minutes after heat is applied. With careful attention to details, this time can be shortened. It has been found that 130 ml. of distillate carry over all of the ammonia even from a steel containing 0.10% nitrogen. A smaller volume is sufficient for low nitrogen steels but, as a precaution, about 130 ml. are regularly distilled over.

At the end of the distillation, the dilute ammonia solution is titrated with 0.00714 *N* sulfuric acid until the faint reddish color of the mixed indicator is again obtained. (The indicator is a solution of 0.075 gram of bromocresol green and 0.05 gram of methyl red in 100 ml. of methanol, which changes color at pH 5.1.) Blanks are run frequently. The blank usually is equivalent to 0.6 to 0.8 ml. of 0.00714 *N* acid. Nitrogen-free water is used. It is prepared by adding 4 grams of sodium hydroxide and 2 grams of Devarda's alloy to approximately 12 liters of distilled water and digesting the mixture at 90° to 95° C. for 12 to 16 hours. If this method is used, it is not necessary to redistill the water. The 33% sodium hydroxide solution is prepared in a similar manner.

A natural question is, "Does the mere solution of the sample convert all of the nitrogen to ammonium salts?" Many comparisons of results obtained by the above-described simple solution method have been made with results obtained by mild and severe digestion on samples of plain, low-carbon steel. No instances have been found where the results obtained by solution differ more than the experimental error from results obtained by more drastic treatment. Alloy steels require more severe treatment.

When dealing with more complex steels, the sample is dissolved in a sulfuric-phosphoric acid mixture, the insoluble residue is collected on a close filter paper, digested in a sulfuric acid–copper sulfate–potassium sulfate mixture, and added to the filtrate, and total nitrogen is determined by one distillation. This, or recovery of the insoluble residue with the centrifuge and digestion of the insoluble material, is considered the surest method for complete recovery of the nitrogen in complex steels. The method of dissolving a sample in sulfuric-phosphoric acid mixture after the addition of selenium, evaporating to incipient fuming, adding more concentrated sulfuric acid, and then fuming for from 1 to 5 hours has been found frequently to yield low results, particularly on steels containing titanium.

The digestion step with its choice of a great variety of catalysts, temperature boosters, acid mixtures, times of digestion, etc., has been the subject of many investigations and conflicting opinions. It is a step that still remains controversial. It appears now to be well established that the addition of any oxidizing agent to a nitrogen digest may cause an error. This rules out the use of perchloric acid. Fuming with sulfuric acid is likely to cause loss of nitrogen, particularly where temperature boosters like potassium sulfate are used. Where long digestions are employed, the later stages of the digestion may be characterized by a gradual production of ammonium salts from unconverted nitrogen compounds and at the same time a slow loss of nitrogen from the ammonium salts produced earlier. The two simultaneous effects may compensate each other in such a manner as to lead to erroneous conclusions.

The use of selenium and its compounds in the digestion step has been the subject of much conflicting opinion. Selenium appears to be useless in the determination of nitrogen in steel. Tartaric acid, commonly recommended as an aid to distillation, serves no useful purpose and is objectionable in the steam-distillation procedure. The frequently recommended practice of catching the distillate in excess acid is considered the poorest of several possible procedures. For small amounts of nitrogen, a very good practice is to catch the distillate in 10 to 20 ml. of neutral water. For higher amounts of nitrogen, a very good practice is to catch the distillate in a volume of the standard titrating acid slightly less than the total amount needed and then complete the titration with more of the same acid. A practice that is preferred to either of the above is to catch the distillate in a weak solution of boric acid.

Hague stated that the National Bureau of Standards is interested in the determination of nitrogen in a great variety of steels and ferroalloys. Recently, in connection with the effect of nitrogen on the hardenability of steel containing boron, the laboratory was faced with the necessity for making a very large number of such analyses. The most promising procedure from the standpoint of economy of both time and reagents appeared to be some adaptation of the microchemical technique. Eventually a semimicro modification of the Allen method was adopted.

Steam distillation, which has been used by Beeghly (*4*) on a semimicro and by Kempf and Abresch (*8*) on a macro scale, proved the most satisfactory method for recovery of the ammonia obtained by conversion of the nitrides in steel to ammonium salts.

An accurate method for the separation and determination of ammonia could be useful only if reliable methods could be devised to decompose and convert the nitrides in the steel to ammonia. It was to this step in the procedure that most attention was devoted. Decomposition must be carried out by a procedure

depending on the information needed. Frequently all that is required may be obtained by dissolving the sample in acid. In such steels, usually only the nitrogen present as iron nitride is of interest. In other cases, it may be desirable to know how much nitrogen is combined with the different alloying elements. These nitrogen compounds are often affected by heat treatment, so that the proportions that exist can be changed.

As a general procedure, the National Bureau of Standards desires to certify the total nitrogen in a sufficient number of samples so that reasonably accurate values are available to the public for use as reference.

For this purpose, the solution procedure consists of dissolving a 0.5-gram sample in a Vycor micro-Kjeldahl digestion flask over a small flame with 10 ml. of sulfuric acid (1 to 2) containing 1 to 2 drops of hydrofluoric acid (48%) and a few drops of hydrogen peroxide (30%). This mixture then is evaporated over an open flame with a twirling motion until most of the water is driven off. After cooling under tap water, 1 ml. of hydrogen peroxide (30%) is added and the heating is resumed to the point of fumes. The flask is then returned to the digestion rack and digested for 3 to 4 hours at a temperature sufficiently high to give some refluxing action with the sulfuric acid. The flask should be rotated occasionally to prevent excessive caking. Again, the solution is cooled under tap water, 10 ml. of ammonia-free water are added, and the flask is warmed gently to dissolve the iron salts. The solution at this stage is ready for distillation.

For the distillation step the Parnas and Wagner (*9*, *10*) micro-Kjeldahl steam-distillation apparatus is used without modification, except to change the vacuum jacket to a size that will accommodate the amount of sample needed for steel. The chief appeal of this apparatus is the small amount of ammonia-free water it requires per sample. Only 5 to 10 ml. are necessary. The major advantages of the semimicromethod are:

1. A small sample (0.5 to 1.0 gram) is much easier to fume and digest than a large one.
2. The small quantity of iron salts permits a rapid distillation and a reduced time per determination. Not more than 25 ml. of distillate need be collected and this can be done in 4 or 5 minutes.
3. Ease of operation. Difficulties from bumping and mechanical entrainment of alkali are not experienced during distillation.

The distillate containing the ammonia is collected in a 50-ml. borosilicate glass Erlenmeyer flask containing approximately 5 ml. of boric acid (2% solution) containing 4 drops of indicator [5 parts of bromocresol green (0.1 gram dissolved in 100 ml. of 95% ethyl alcohol) mixed with 1 part of methyl red (0.1 gram dissolved in 100 ml. of 95% ethyl alcohol)]. The distillate is titrated with 0.01 *N* hydrochloric acid to a clear pink end point.

Before the first determination, the distillation apparatus is thoroughly steamed out. A blank run is made, preferably by carrying a 0.5-gram sample of known nitrogen content through all steps of the procedure. Normally, a blank equivalent to 0.15 ml. of 0.01 *N* hydrochloric acid will be obtained.

The titration procedure was adapted primarily for stainless and alloy steels where a relatively wide range of nitrogen contents (approximately 0.01 to 0.25%) is encountered and a nominal accuracy in the order of ±0.002% is acceptable. It is not convenient to adapt the photometric procedure to such a wide concentration range. For lower nitrogen contents, a photometric procedure utilizing the Nessler reaction in the manner described by Beeghly (*4*) has definite advantages in its absolute accuracy.

The semimicroprocedure has been in use for 8 to 10 years and results obtained with it have been compared many times with those obtained by the vacuum fusion procedure on the same material. With suitable precautions, they agree well. Steels containing columbium or titanium must be heated to a higher temperature than carbon steels in the fusion procedure, if all of the nitrogen is to be recovered. In the solution step of the semimicromethod, the digestion must be made carefully or only part of the nitrogen will be converted to the soluble form in steels containing such elements as columbium or titanium. If the characteristics of the steel are well known, the digestion with a sulfuric-hydrofluoric acid mixture in the presence of hydrogen peroxide may be shortened in many cases. Where the composition or heat treatment history is not known, this is not advisable if a total nitrogen value is desired.

In preparing the specimen for analysis, it has been found advisable to descale the specimen with acid before milling rather than by grinding, as is frequently done. The grinding operation may result in a substantial increase in the nitrogen content of some grades, especially if a large surface is involved.

Summary. The consensus of the panel was that the method for determining nitrogen must be adapted to the purpose for which the analysis is needed. A practice acceptable for one grade may not be acceptable at all for another. The most economical method can be used only if the characteristics of the product are known. The other alternative is to use a method that will get the total nitrogen content in anything that comes along. Such methods are available but, for day to day use, they are more expensive and, consequently, it is desirable, where possible, to use the simplest method that will enable the necessary results to be obtained for a particular plant.

Hydrogen peroxide (30%), when used, must be checked carefully for its nitrogen content and added in measured quantities to avoid excessive and erratic blanks. Considerable variations in the nitrogen contents of commercial lots of peroxide exist. Some lots are not acceptable for the nitrogen determination. Use of peroxide for this purpose is comparatively recent and present AMERICAN CHEMICAL SOCIETY reagent specifications (*5*) allow more ammonia nitrogen in peroxide than can be tolerated for the nitrogen determination.

Use of sulfates in the digestion step is a source of error if excessive amounts are used. For a 5-gram sample, 20 ml. of sulfuric acid, 10 grams of potassium sulfate, and 1 gram of copper sulfate were considered practical maxima. With larger proportions of sulfate to acid, loss of nitrogen occurs. Metallic copper in larger quantities may be used as a substitute for copper sulfate. In general, use of strongly oxidizing acids such as perchloric or drastic oxidation was considered to cause loss of nitrogen.

Time and difficulty in preparing ammonia-free water considered necessary to the determination of nitrogen in most steels can be avoided by passing distilled water over an ion exchange resin column. A mixture of 2 parts of Amberlite IRA 400 with 1 part of Amberlite IR 120 may be used to produce 5 gallons or more per hour of ammonia-free water.

Where the titration procedure is used, absorption of the ammonia in boric acid appears to be preferred because more consistent results are obtained. For low nitrogen contents, no absorbent is necessary; for high nitrogen contents absorption in excess acid is satisfactory. Use of electrometric titration in the semimicroprocedure with the ammonia absorbed in excess acid was suggested. By adding an excess of potassium iodate and back-titrating, a very sharp end point can be obtained.

The steam-distillation procedure was in most general use for separating the ammonia from alkaline solution. The distillation step was considered the easiest part of the determination. The method of Gotta and Seehof (*6*), in which the iron was precipitated as the hydroxide and filtered off and the ammonia content was determined directly on the filtrate, was reported as unsatisfactory. The vacuum fusion procedure was not reported to to be in regular use for the determination of nitrogen.

DETERMINATION OF SULFUR

The moderator opened the discussion, stating that the sulfur content is a part of the specifications under which steel is bought and sold. Consequently, its determination has been required at certain stages in the manufacture of all steel for many years. Recently there has been a renewed interest in the determination of sulfur occasioned by the development of new alloys, for which previously accepted methods have many disadvantages.

The most common procedures are:

1. Decomposition of the steel, so that all the sulfur is converted to the sulfate ion which is separated from the iron, precipitated as barium sulfate, ignited, and weighed.

2. Decomposition of the steel, so that all the sulfur is evolved from the iron as hydrogen sulfide which is absorbed and finally estimated by titration.
3. Ignition of the steel sample at a high temperature in an atmosphere of oxygen, absorption of the oxides of sulfur from the combustion products, and final estimation of the sulfur by titration.

The latter two methods, though widely used, are empirical at present.

Sulfur Panel. Members of the sulfur panel then described the methods used in their laboratories.

Mills stated that gravimetric determination of sulfur may be carried out by dissolving the specimen in nitric acid, evaporating the resulting solution with hydrochloric acid, and reducing the iron to the ferrous state with zinc, after which the sulfur is precipitated from the filtered solution by addition of barium chloride. The precipitated sulfate is collected on a filter, ignited, and weighed. Elements such as molybdenum, tungsten, and chromium in the oxidized state, and nitrates will contaminate the barium sulfate if present at the time of precipitation.

Another gravimetric procedure, especially designed for alloy steels but also applicable to carbon steels, utilizes the reaction of copper-potassium chloride to dissolve iron and alloying elements from the steel, leaving the sulfur in the insoluble residue chiefly as copper sulfide together with graphitic carbon and insoluble carbides of chromium, vanadium, etc. This insoluble residue is collected on a filter and oxidized with nitric acid and potassium chlorate and the sulfur is precipitated as barium sulfate after expulsion of all nitrates.

The evolution method has been widely used because it is rapid and simple and, under properly controlled conditions, will give satisfactory results on plain carbon and many alloy steels. It is not applicable to steels containing molybdenum or titanium. The evolution method is empirical and variations in details of the procedure will yield inaccurate results.

By this method, a 5-gram sample is dissolved with 90 ml. of hydrochloric acid (1 to 1) in a dry Johnson sulfur flask of 250-ml. capacity. The evolved gases are conducted into approximately 250 ml. of water containing 15 ml. of ammoniacal zinc sulfate solution (200 grams of zinc sulfate heptahydrate plus 1 liter of water and 1 liter of ammonium hydroxide) in a tall-form beaker so shaped that the absorbent has a depth of at least 6.5 cm. The beaker should be kept in a cooling tray during the solution reaction. The flask is heated gently until the sample is in solution and then boiled slowly until the delivery tube extending into the absorbent becomes hot from the evolved steam. The delivery tube is then disconnected and left in the beaker, 2 to 3 ml. of arrowroot starch are added, and the absorbent is acidified with 90 ml. of hydrochloric acid (1 to 1) and titrated with standard potassium iodate (0.0312 *N*) to a permanent blue color. The starch is prepared by suspending 10 grams of arrowroot starch in cold water, adding 1 liter of boiling distilled water, and digesting at the boiling temperature until the starch dissolves. Then the solution is cooled, 10 ml. of saturated zinc chloride and 15 grams of ammonium chloride are added, and the solutions are allowed to stand 48 hours; the clear solution is then decanted into a clean glass bottle and 5 grams of potassium iodide are added for each liter of clear solution; when 3 ml. of this starch solution are used a deep blue color should be obtained with 0.2 ml. or less of the standard potassium iodate.

The combustion procedure has rapidly displaced both the evolution and the much slower gravimetric method for the determination of sulfur in many ferrous materials. Like the evolution method, it is still empirical, but accurate results can be obtained rapidly once the method is standardized and carefully followed. A single determination, even on alloy steels, can be made in 3 to 4 minutes. The details of both the technique and the apparatus differ from one laboratory to another. In the procedure that follows, approximately 80% of the total sulfur is absorbed as sulfur dioxide and titrated; the remaining 20% is not absorbed and does not enter into the titration reaction.

A 1-gram sample is placed in a refractory-type combustion boat; the millings are spread evenly over about two thirds the length of the boat and covered evenly with a thin layer (0.1 to 0.2 gram) of 30-mesh tin. With the oxygen flowing through the tube, the absorption vessel is rinsed with distilled water and allowed to drain, and the stopcock at the bottom of the absorption vessel is closed. Then 30 ml. of starch solution, 1 ml. of hydrochloric acid (1 to 1), and sufficient standard potassium iodate (about 0.3 ml.) to produce a blue color are added to the absorption vessel. The two-way stopcock controlling the flow of oxygen is adjusted so that the oxygen exhausts to the air and the combustion boat and sample are introduced into the thimble which is centered in the hot zone inside the combustion tube. The temperature in the tube should be controlled (± 25° F.) by means of an automatic potentiometer. A temperature of 2400° F. (1316° C.) is used for cast irons, carbon steels, or low alloy steels; for high alloy steels, the temperature should be 2600° F. (1427° C.). The stopper is immediately replaced and the sample preheated for 1 minute, after which the flow of oxygen through the tube is started. As the sample burns, the evolved sulfur dioxide reacts with the iodate and the blue color begins to disappear. More standard iodate must be added at a rate sufficient barely to maintain a blue color. When an end point is obtained that does not fade in 30 seconds (60 seconds for high alloy steels), the determination is complete. The solution is drained and the absorption vessel rinsed, with the oxygen still flowing, after which the apparatus is ready for the next determination.

The sulfur content is calculated by multiplying the volume of standard iodate used in the titration by a factor which has been established by carrying the steel samples of known sulfur content through exactly the same procedure.

A zirconium oxide combustion tube 1 inch (2.54 cm.) in inside diameter and 27 inches (68.6 cm.) long is used. It is positioned in the furnace so that the exit end extends approximately 5 inches (12.7 cm.). The accumulated oxides should be scraped from the exit end every 8 hours (every 30 to 35 determinations if cast iron is run) if the furnace is in continuous use. The exit end should be drawn into the hot zone of the furnace and burned out at weekly intervals. A furnace with a hot zone approximately 9 inches (22.9 cm.) long and capable of continuous operation at 2550° F. (1399° C.) may be used. Sulfur-free boats must be stored in closed containers to prevent absorption of sulfur-containing gases from the atmosphere. Blanks should be run on each lot of boats and, if necessary, they must be preignited 3 to 4 hours to remove sulfur contamination. The dust (metal oxides) formed during combustion and not retained by the Alundum thimble (80 mm. long and 25 mm. in diameter, coarse porosity) surrounding the sample boat is retained by a glass wool plug inserted in the combustion tube just inside the exit end. A new filter should be conditioned by burning at least two unweighed samples before running the first standard. A new glass wool plug should be inserted every 8 hours if the apparatus is in continuous use.

The method described by Parsons was suggested by Eugene Bennett of the Union Carbide Co., Niagara Falls, in April 1944. The method of sulfur analysis was used as described, except that an Alundum thimble cemented to a refractory tube and filled with asbestos was used to conduct the evolved gases to the titration vessel. Bennett was using a photoelectric device for determining the end point of the iodine-starch titration. After some experimentation, the Alundum thimble, which was expensive, was discarded and replaced with a refractory thimble made from insulating brick at a cost of about 3 cents per thimble. The purpose of the thimble is to prevent the passage of any ferric oxide to the cooler parts of the system, where some of the sulfur dioxide might be converted to sulfur trioxide.

At a later date, the temperature of the furnace was increased to 2550° F. (1399° C.) and the factor for the conversion of sulfur to dioxide was increased to between 90 and 91% of the theoretical titer value of the iodine solution. At this time the use of tin shot as an accelerator was discontinued with a consequent reduction in the amount of red oxide of iron evolved. Analytical results for sulfur obtained were fairly consistent, particularly in the higher sulfur ranges.

During this period, the size of the sample was held at 1 gram for each sulfur determination. By further reducing the size of the sample to 0.5 gram for sulfur under 0.15% and 0.25 gram for sulfur over 0.15% and using a standard potassium iodate solution half the strength formerly used, it was noted that only a small amount of ferric oxide was evolved during the combustion

and that the operators could titrate to a pale blue end point with excellent precision over the entire sulfur range (0.01 to 0.30%).

Further work at elevated temperatures (2650° to 2750° F.) (1454° to 1510° C.) indicated that very near (about 98%) the theoretical sulfur titer could be obtained, but the necessarily frequent tube replacements and the lack of sufficient refractoriness in the boats then available made the method too costly for routine determinations. The tubes had a tendency to soften and become bowed at these temperatures, while the boats would react with the slag and at times become almost shapeless masses of porcelain and slag. Consequently, the method now in use at Lackawanna was adopted, the furnace being held at 2550° F. (1399° C.), using porcelain boats and a commercially available titration assembly designed for the iodometric determination of sulfur.

APPARATUS. Furnace. Any suitable furnace that will maintain a temperature of 2550° F. (1399° C.).

Combustion Tube. A tube 30 inches (76.2 cm.) long and 1 inch (2.54 cm.) in inside diameter, of the McDanel type, is used.

Titration Assembly. A commercially available assembly supplied for the iodometric method is used. The ends of the combustion tube are wrapped with a coil of 0.25-inch (6.3-mm.) diameter copper tubing through which water flows to protect the rubber stoppers and absorbent solution from excessive heat.

Oxygen Flow. The flow of oxygen through the system is adjusted by means of a needle valve, so that the flow through the titration vessel is fairly rapid. An excessive flow rate must be avoided or some of the starch and iodate solution will be sprayed over the top of the titration vessel.

Filter Assembly. The filter proper is a cylinder made from insulation brick (such as Armstrong No. 28) 1 inch (2.54 cm.) in diameter and 2 inches (5.08 cm.) long, with a porosity of between 60 and 70%. At one end of the cylinder is drilled a hole 0.75 inch (1.9 cm.) deep to receive an Alundum tube 0.375 inch (6.95 cm.) in outside diameter and 12 inches (30.5 cm.) long. A baffle ring made of Transite is strung on the tube and placed next to the stopper to protect it from excessive heat. This ring is 0.9375 inch (2.4 cm.) in diameter with a 0.375-inch (0.95-cm.) hole drilled through the center. The thimble itself is ground off at one end to a blunt point and notched to offer a larger filter area to the evolved gases. The over-all length of the thimble assembly is approximately 13.5 inches (34.3 cm.) The tube is cemented to the filter using Alundum high temperature cement moistened with water and a few drops of sodium silicate solution. The assembly is allowed to dry at room temperature and, before using, the refractory end of the thimble assembly is heated to a red heat for about 30 minutes to drive out any moisture and any sulfur that may remain in the cement.

The refractory thimble is placed in the hot zone of the combustion tube, so that it is uniformly heated throughout. A thimble that is partially cooled will give low sulfur results. The end of the combustion tube containing the filter assembly should not extend beyond the furnace more than 8 inches (20.3 cm.). To prevent excessive accumulation of the slag on the thimble, the combustion boat is placed in the tube approximately 1 inch (2.54 cm.) from the hot thimble. The thimbles are replaced when the slag accumulation interferes with the oxygen flow.

PROCEDURE. The sample used varies according to the sulfur content of the steel. For steels containing 0.01 to 0.15% sulfur, a 0.5-gram sample is used; from 0.15 to 0.35%, a 0.2-gram sample is preferable. For pig iron or cast iron, material passed through a 10-mesh sieve and caught on a 40-mesh sieve is satisfactory. All steel samples should pass through a 10-mesh sieve and be caught on a 60-mesh sieve. Finely powdered samples yield erratic results unless burned with steels of known sulfur content. A blank according to the sulfur content of the steel used must be subtracted from the results so obtained.

A sample of suitable size is weighed into regular porcelain boats. The boat is covered and preheated in the combustion tube for at least 1 minute. The tube is stoppered and the flow of oxygen started through the train. During the preheating period the titration vessel is filled to the mark with the starch solution. Then 1 ml. of hydrochloric acid and at least a sufficient amount of standard iodate solution to give a deep blue color are added. With the oxygen passing through the train and as the blue color of the starch solution begins to fade, standard iodate is carefully added from the buret until a permanent blue color is formed. The iodate solution is standardized by means of a standard steel and all titrations are carried out to a light blue end point. When the approximate sulfur content of the steel is known, 60 to 80% of the required amount of iodate may be added at the start of the titration. This insures the operator against too rapid bleaching effect of the sulfur dioxide on the starch solution and permits him to approach the end point more gradually.

The importance of a rapid but not excessive flow of oxygen (1000 to 1200 ml. per minute) cannot be overstressed. A temperature of 2550° F. (1399° C.) is maintained in the furnace. No tin accelerator is necessary for plain carbon steel. For steels of the heat-resisting type, the temperature of the furnace should be raised to 2650° F. (1454° C.) or 2700° F. (1482° C.). Tin or some other accelerator should be used; boats of exceptional quality are desirable; tube life is very short. The standard potassium iodate solution used at the lower temperatures will consistently give high results, indicating that a theoretical or near-theoretical titer should be used.

Slag accumulation in the combustion tube should be watched rather closely. Results are apt to be a little low when large amounts of iron oxide are present. Furthermore, the slag has a tendency to permeate the walls of the tube, ultimately rendering it useless.

Saxer reported that the determination of sulfur by combustion was practiced in Germany prior to 1920. Seuthe (*12*) described a procedure in which the sulfur dioxide was absorbed in hydrogen peroxide, after which an excess 0.05 *N* sodium hydroxide containing methyl red was added to the solution and the excess was titrated with 0.05 *N* sulfuric acid. The practice of absorbing sulfur dioxide in alkaline peroxide solution has been generally abandoned because carbon dioxide interferes with the end point. Pohl (*11*) developed a photometric method based on the reduction of fuchsin solution by sulfur dioxide. This method also was empirical and never found widespread acceptance. The iodometric combustion method found most general acceptance because of the sharp end point that could be obtained with the blue starch-iodide complex. The titration depends on the reducing power of sulfur dioxide. But as not all the sulfur is evolved in this form, the method is empirical.

At the Otis Works, considerable experimental work has been done with both the iodometric and the alkaline hydrogen peroxide methods. Results were disappointing. Later an acid hydrogen peroxide absorbent was tried in an effort to devise a stoichiometric method.

Combustion was carried out at a temperature of 2600° F. (1427° C.) with the specimen boat contained in a thimble with two 0.046875-inch (1.2-mm.) holes drilled in the closed end. The thimble was located in the central portion of the hot zone of the combustion tube. Use of any additional filter was found to be unnecessary.

The combustion gases were conducted into the absorbing solution with a gas dispersion tube of the type used by Woodward and Wolthorn (*13*). The absorbent consisted of a saturated solution of potassium chloride containing 35 ml. of hydrogen peroxide (30%) and 1.5 ml. of a wetting agent per liter. The solution was titrated electrometrically to an end point at pH 5.0.

Summary. All members of the panel reported use of temperatures in excess of 2500° F. (1399° C.). The life of combustion tubes at such temperatures is short. Induction heating was suggested as one method of avoiding expensive tube replacements; the experience of one person in analyzing all types of stainless steels and slags for sulfur indicated that induction heating was a satisfactory substitute for the resistance-type furnace. The consensus was that induction heating will eliminate many serious refractory problems and will be feasible if a satisfactory recovery of sulfur can be obtained with this apparatus. Several commercial induction heating units for use in the carbon determination have recently been made available.

For ferroalloys, Furey reported use of the combustion method for approximately 95% of alloys encountered with a recovery of 100% of the sulfur, so that an empirical factor is not necessary. An elapsed time of 10 minutes per determination by combustion compared to 72 hours for ferrotungsten by the usual procedure was reported. Accuracy and reproducibility are as good as and frequently better than with the gravimetric procedure. A temperature of 2700° F. (1482° C.) is used. This causes combustion

tubes to sag and requires frequent replacement of the furnace insulation. The method, nevertheless, is cheaper and more reliable than those previously used for chromium alloys containing titanium and zirconium, which hold sulfur very tenaciously. Sulfur may be precipitated from high-chrome solutions as the sulfate and dried, the impure precipitate placed in the furnace, and the sulfur burned off. Ore tailings containing as much as 8.5% sulfur and 2% arsenic have been run and results obtained in excellent agreement with those obtained by the gravimetric method.

With ferrotungsten and iron ores, an accelerator has not been found necessary; for ferrochrome, 30-mesh tin is required. Open hearth slags are run successfully using a low-sulfur steel standard as a bedding material. The exothermic reaction of the steel with oxygen appears to improve recovery of the sulfur as sulfur dioxide.

The consensus of the panel and audience was that an empirical factor based on a sulfur recovery in the order of 80 to 90% was necessary at present in analyzing steels routinely on a 24-hour-a-day basis. The experience of some persons was that this factor varied from day to day; others do not encounter this day-to-day variation but find a variation from one sulfur range to another—i.e., the factor for an 0.030 to 0.040% sulfur range is different from that for a 0.10 to 0.15% sulfur range.

Apparently, there remain details of the procedure not yet well enough understood to be standardized. It has not been established with certainty, for example, whether recovery of all the sulfur as sulfur dioxide depends on use of high temperatures or on prevention of condensation of iron oxide in the cooler portion of the tube. Methods that will operate regardless of the form in which the sulfur is evolved seemingly have not been completely investigated. Exploration of these and other aspects of the procedure remains a challenge to the analytical chemist. In the meantime, the combustion method is being used empirically but successfully in many different laboratories and by different operators.

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Coulometric Titration of Manganese in the Submicrogram Range

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Recent work on a sensitive electrometric end-point procedure indicated that the range of titrimetric analysis could be considerably extended. The use of this end point, in conjunction with coulometric generation of ferrous ion, allowed permanganate solutions to be titrated in the parts per trillion range. Solutions of 0.001 to 0.0005 microgram of manganese per milliliter could be titrated with an accuracy of about 5%. With more concentrated solutions the error was considerably less. Coulometric titrations using generation currents of a few microamperes have been found feasible. To obtain a satisfactory end point in titrations at such dilutions, diffusion currents at a large stationary electrode were measured to 50 micromicroamperes. The use of these techniques has made possible the titration of solutions at greater dilutions than was possible by techniques previously in use.

COULOMETRIC methods have offered the possibility of extending titrimetric procedures to a concentration range unattainable by conventional titration. Currents of the order of 60 electrons a second can be measured using modern electrometer tubes (*3*). Hence, it seems that there is no practical minimum to the magnitude of currents that can be used to generate reagents coulometrically. The limitations of such procedures lie in the detection of the end point and possibly even the chemistry of the systems involved. A recently developed end-point procedure has been applied to the titration of ferrous ion with electrically generated ceric sulfate (*2*), and the titration of vanadium in uranium with electrically generated ferrous sulfate (*4*). In the present work, a further investigation of the end-point method has been undertaken, and the method extended into the submicrogram range.

A potentiometric-type procedure has been described which uses an amperometric indication of the potential of the solution (*2*). A reference potential is chosen near the point of steepest slope on the potentiometric titration curve in a fashion similar to that of Muller (*5*). The solution is then titrated to the particular reference potential chosen. An ordinary amperometric circuit using a large stationary platinum electrode shows when the reference potential is reached during the titration. The desired reference potential is impressed upon the indicator electrode by the voltage supply shown in Figure 1. When no current flows in the indicator circuit, it must be assumed that the potential impressed upon the electrode and the potential of the solution are the same. At any other solution potential, a diffusion current will be noted in the indicator circuit. Thus, the titration is carried out until there is zero diffusion current, which indicates that the potential of the solution has reached the chosen reference potential. By pretitrating the reagents used to the reference potential before addition of the unknown, much more accurate results could be obtained, and the method could be applied to solutions of much greater dilution. This also made the exact choice of a reference potential less important (*2*). Another advantage of this proce-

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dure was that the effects of impurities in the reagents were minimized. In fact, the reagents could be made up in tap water and the correct results obtained in the submicrogram range. This is advantageous because it eliminates many of the tedious precautions necessary in conventional trace analysis.

Using a sensitive galvanometer in the indicator circuit, very large deflections could be obtained for relatively small amounts of material. For example, 1 microgram of manganese as permanganate ion gave a galvanometer deflection equivalent to 700 meters when an indicator electrode of 3 sq. cm. was used. This gave a sensitivity of about 10^{-6} microgram, or 1 micromicrogram.

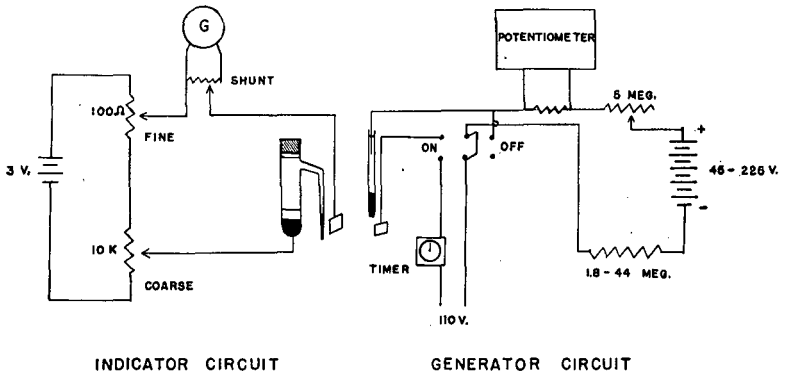

Figure 1. Wiring Diagram

As comparatively high diffusion currents were obtained using the large stationary electrode, the amount of material electrolyzed at the indicator electrode was at times enough to cause low results. This effect was decreased by using smaller electrodes with the larger samples.

In macrotitrations of potassium permanganate with ferrous sulfate, the potential of the solution at the end point is about 1.04 volts versus the hydrogen electrode. In titrations in the microgram range when this voltage was used as an end-point reference, low results were obtained. According to the Nernst equation this would be the case if the correct end point voltage was lower than 1.04 volts. It was found that any reference potential below 0.89 volt gave the correct titration value if the solution was pretitrated to the chosen value before addition of the unknown as previously outlined.

Although any reference voltage below 0.89 volt may be used, other factors influence the choice of this potential. The sensitivity of the end point varies considerably with the voltage applied. This is to be expected, as the slope of the potentiometric curve is different at different voltages. On the steep portion of the potentiometric curve, a greater voltage change and hence a greater sensitivity are realized for the addition of a quantity of permanaganate. On the flat portions of the curve where the solution is well poised, only small voltage changes can be realized. This change in sensitivity with potential is shown in Table I, in which the galvanometer deflection per microgram of manganese is shown for the 0.1 sq. cm. electrode.

Table I. Sensitivity Change

Reference Potential	Sensitivity, Mm./γ
0.88	11,500
0.86	4,200
0.80	3,300
0.75	930

One other factor influencing the choice of a reference potential is the stability of the solutions when adjusted to the chosen voltage. For example, when the solution of ferric sulfate was adjusted to a potential of 0.75 volt (by the generation of ferrous), a rapid drift of the indicating galvanometer was noted. This drift was in the direction of an increase in voltage or oxidizing power, and was believed caused by the air oxidation of the ferrous ions in solution. When the solution was adjusted to a higher voltage, the drift disappeared, because the solution became more difficult to oxidize. By choosing a voltage above the point at which the solution would react with air, it was possible to carry out the titrations without excluding air. Pure ferrous sulfate solutions in air, at these dilutions, would probably be extremely unstable. In view of the above facts, a potential of about 0.87 volt was chosen.

The buffering of the permanganate with manganous ion was found to be advantageous. Steadier diffusion currents and more accurate results were obtained by the addition of a large excess of divalent manganese. As a large excess of both ferric ion and manganous ion is present, the addition of the permanganate sample to this poised solution changes the potential only slightly. The addition of a sample of 0.01 microgram changed the potential of the solution about 10^{-4} volt. However, as a very sensitive galvanometer was used, this slight change in potential was amplified to a satisfactory deflection. Because of the small magnitude of the voltages measured, the voltage impressed upon the indicator electrode should be kept constant to within a few microvolts during the titration period.

When the solution of ferric ion is adjusted to 0.87 volt, a rather large amount of ferrous ion is present in solution compared to the size of the samples of permanganate added. When the permanganate is added it is believed that reaction with the ferrous ion present immediately takes place. The titration then consists of merely adjusting the Fe^{+++}/Fe^{++} ratio to its original value. This possibility might be advantageous in the titration of solutions which are unstable in the titration medium, or require an excess of reagent for rapid reaction.

Thermostating the titration cell was helpful in the submicrogram range. It is believed that the difficulty necessitating temperature control is not caused by the dependence of the diffusion coefficients on temperature, but the variance of the potential of the solution with temperature according to the Nernst equation. As potential changes of a few microvolts are probably

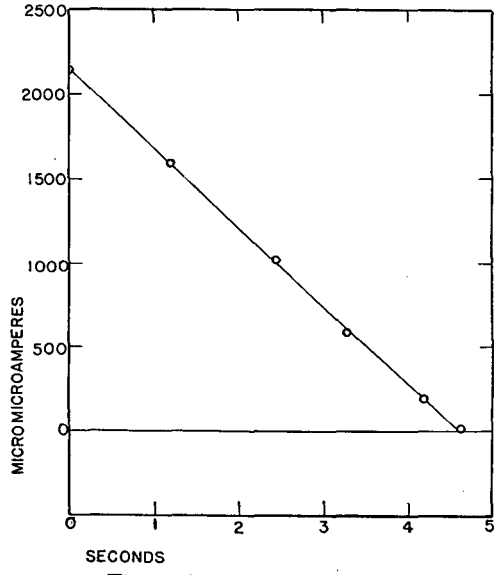

Figure 2. Titration Curve

Table II. Coulometric Titration of Manganese

Mn Taken, γ	Mn Found, γ	Error, %	Approximate Generating Current, μa.
1.201	1.189	1.0	50
1.091	1.096	0.5	
1.328	1.310	1.4	
1.227	1.229	0.2	
1.196	1.216	1.7	
0.712	0.721	1.3	
0.501	0.494	1.4	
0.516	0.515	0.2	
0.543	0.536	1.1	
0.484	0.492	1.7	
0.197	0.187	5.0	10
0.171	0.171	0.0	
0.166	0.157	5.6	
0.146	0.155	6.4	
0.199	0.204	2.5	
0.215	0.213	1.0	
0.173	0.176	1.8	
0.192	0.205	6.9	
0.153	0.157	2.6	
0.0786	0.0779	0.9	5
0.0419	0.0429	2.4	
0.0384	0.0380	1.1	
0.0483	0.0488	1.0	
0.0511	0.0505	1.2	
0.0369	0.0373	1.11	
0.0099	0.0092	7.1	
0.0076	0.0084	9.2	
0.0033	0.0030	9.1	

significant, this factor could cause gross errors unless the temperature was controlled. However, only temperature changes during the course of the titration would cause difficulty.

At the beginning of this work, a mercurous sulfate half-cell was used as a reference electrode. This electrode was found to have disadvantages in submicrogram titrations. Because small currents were continually drawn through the cell, rather large fluctuations would occur in the e.m.f. of the cell. The second disadvantage was the comparatively high solubility of mercurous sulfate. Slow diffusion of mercurous ions through the agar plug caused difficulty in the permanganate titration. To avoid these difficulties, a saturated lead amalgam–lead sulfate electrode in 0.5 N sulfuric acid was used. This half-cell maintained a rather constant e.m.f. (−0.27 volt) and no oxidizible ions were introduced into the titration vessel. For this reason, the lead amalgam–lead sulfate electrode is recommended for microelectrometric titration. Care should be taken in the preparation of this electrode; especially, the platinum wire lead under the mercury should be dry (*1*).

In order to obtain known samples of 1 microgram or less, solutions down to 10^{-4} N potassium permanganate were prepared daily by diluting a stock 0.1 N solution. For samples less than 0.1 microgram, quantities as small as 1 mg. of 10^{-4} N solution were measured into the solution to be titrated by means of a weight buret constructed from a 1-ml. hypodermic syringe. More dilute standard solutions were not prepared because of two possible sources of error: the apparent presence of a small amount (10^{-6} or 10^{-7} N) of reducing agent in the distilled water, and the fact that by storing the solution at higher concentrations, the possibility of significant adsorption on the surface of the glass vessels was minimized.

APPARATUS

The titration cell was similar to one previously described (*2*) except it was equipped with a water jacket to maintain the temperature to within 0.1° C. The capacity of the cell was about 7 ml. The generator cathode was of platinum-iridium foil, 1 sq. cm. in area. The anode compartment of the generator circuit consisted of glass tubing 3 mm. in diameter, isolated by a 4% agar–2% ammonium sulfate plug, and containing 0.1 N sulfuric acid. A small platinum wire was used as the anode. The indicator circuit consisted of a platinum-iridium foil electrode, and a saturated lead amalgam–lead sulfate reference electrode, as shown in Figure 1. Three indicator electrodes of different areas (3, 0.8, and 0.1 sq. cm.^{2}) were used, so that a diffusion current of desirable magnitude could be obtained. The solution was stirred by means of a magnetic stirrer.

ELECTRICAL CIRCUIT

Because the generating currents used in this work were less than 50 microamperes, a constant voltage supply was used as a constant current source (*6*). Five small-capacity 45-volt batteries were used as the generating current source, as shown in Figure 1. The current was measured by taking the IR drop across a standard resistance with a potentiometer. The time was measured with a synchronous motor clock (Standard Time Co., S-60). The galvanometer used was a Leeds & Northrup HS type with a sensitivity of 10^{-5} microampere per millimeter, equipped with an Ayrton shunt (ratios 1 to 0.0001). The resistance of the indicator circuit should be as low as possible to increase the sensitivity. Care must be taken that all the connections are sound.

REAGENTS

The ferrous ion was generated from a 0.01 N solution of ferric ammonium sulfate. A 0.01 M solution of manganous sulfate was used to decrease the potential of the permanganate system.

The potassium permanganate solution was standardized against primary standard ethylenediamine ferrous sulfate and was found to be 0.1231 N.

PROCEDURE

About 5 ml. of 0.01 N ferric ammonium sulfate and 0.2 ml. of 0.01 N manganous sulfate were added to the titration cell. The potential of this solution is usually greater than the reference voltage, 0.87 volt. The ferric ion solution was then brought to the reference point by generating the required amount of ferrous ion. After the potential was adjusted, the unknown solution of permanganate ion was added. The timer was reset and ferrous ion generated in appropriate intervals until the galvanometer returned to zero. The diffusion current reached equilibrium in about a minute in the vicinity of the end point. Rather than adjustment of the current exactly to zero, some point near zero current may be used as the reference point. The curves were not plotted, but the return to the original reference potential was taken as the end point. The titration curve for a sample of 0.003 microgram is shown in Figure 2. If the samples were titrated just to the end point, additional samples could be added to the same solutions.

RESULTS

The results of this work are shown in Table II.

ACKNOWLEDGMENT

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Extraction and Determination of Cholesterol in Adrenal Tissue

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An inexpensive and convenient method for the extraction of small quantities of cholesterol from tissue preparation is needed. The procedure developed involves the solvent extraction of a dried tissue preparation. Paper partition chromatography is used rather than digitonide precipitation for the actual separation of the cholesterol. The cholesterol is determined using the Liebermann-Burchard reaction.

IN THE course of in vitro studies on the metabolism of adrenal steroids (*4*), a method was developed for the convenient extraction of cholesterol from tissue preparations. For the eventual determination of cholesterol, the usual Liebermann-Burchard reaction was used.

The salient features of the method are solvent extraction of the dried tissue preparation and then paper chromatography in lieu of digitonide precipitation for the actual separation of the cholesterol.

REAGENTS

Chloroform, washed with water five times, dried over calcium chloride, and distilled. Kept shielded from light.

Liebermann-Burchard reagent, as described by Kingsley and Schaffert (*3*).

Extraction solvent, a 2:1:1 mixture of chloroform–absolute ethyl alcohol–redistilled acetone.

PROCEDURE

A. Extraction of Steroid. An aliquot of the tissue homogenate, or of a complete incubation mixture, is transferred to a short cotton roll of the type used for dental packings. In transfer, the tip of the pipet is applied to the open end of the cotton. This will allow particulate matter from the homogenate to be absorbed into the interior of the roll and circumvent its possible dislodgment during subsequent manipulations. The cotton rolls have previously been exhaustively extracted with chloroform in an all-glass Soxhlet apparatus. For convenience, the cotton rolls are impinged vertically upon sharp glass points projecting from the surface of a glass plate. The rolls are always handled with forceps.

After transfer of the aliquot, the rolls are dried in an air oven at 50° C., just to dryness, and then placed in a vacuum oven at 50° C. for 1 hour. After drying, the cotton rolls are extracted with the chloroform–ethyl alcohol–acetone mixture in 10-ml. micro-Soxhlet extractors for 3 hours on a steam bath. The entire apparatus is of glass, with a calcium chloride drying tube inserted into the ground glass joint at the top of the condenser. Chloroform alone is not used in this extraction, if it is desired to extract not only the cholesterol but other steroids not so readily soluble in this solvent. This procedure removes all the Liebermann-Burchard positive material from the cotton rolls as determined by direct test.

The extracts are cooled, transferred to 25-ml. beakers, and evaporated to dryness on a 50° C. sand bath. To prevent creeping, the solvent vapor is drawn off by means of a water aspirator. When many samples are run at one time, a glass vacuum manifold is used.

In order to obtain a true total cholesterol value, it is necessary to hydrolyze the cholesterol esters present, as these give a more intense Liebermann-Burchard reaction than free cholesterol. The method used is outlined by Gershberg and Farber (*1*). In application, 3 ml. of 1 to 1 acetone–95% ethyl alcohol are added to each beaker, followed by 0.2 ml. of 15% potassium hydroxide. The beakers are set in a 50° C. air oven for 1.75 hours. The alkali is neutralized with the requisite quantity of dilute hydrochloric acid, after which the mixture is taken to dryness on the 50° sand bath.

After cooling, the desired volume of solvent is added to the residue, which is stirred up rapidly and carefully with a pointed glass rod. Finally an aliquot is transferred to a filter paper strip for chromatography. Because of the volatility of the solvents employed, no more than 30 seconds is permitted to elapse between the addition of solvent to the residue and the withdrawal of an aliquot for chromatography.

Table I. Precision and Recovery

Recovery of Cholesterol from Paper Strips

No. of Detns.	Cholesterol, γ Initial	Cholesterol, γ Recovered	% Recovery, Av.
3	200	217	109
3	160	161	100

Addition of Known Amount of Cholesterol to Adrenal Homogenate

Original Homogenate	Cholesterol Values, γ: Homogenate with 100γ added	Difference	% Recovery
2220	2318	98	98

Over-All Precision

No. of Detns.	Cholesterol, γ per Flask	Relative Standard Deviation
4	2051 ± 47	0.04
3	1737 ± 169	0.10
4	1693 ± 69	0.06
3	2318 ± 40	0.03
3	2313 ± 184	0.09
3	2118 ± 10	0.01

Precision for Direct Extraction

No. of Detns.	Cholesterol, γ per 0.2 Ml. of Aliquot	Relative Standard Deviation
5	488 ± 5	0.01
5	276 ± 7	0.03
3	188 ± 8	0.04
2	191 ± 1	0.01
3	153 ± 4	0.02

Extraction Directly from Adrenal Gland. The adrenals are sliced and homogenized directly with 5 ml. of 1 to 1 acetone–95% ethyl alcohol per 200 mg. of tissue. The homogenate is heated to boiling, rehomogenized briefly, transferred to a 12-ml. centrifuge tube, and centrifuged for 5 minutes at low speed in a clinical centrifuge. The supernatant liquid is poured off into a 25-ml. beaker, the residue is washed with three 1-ml. portions of solvent, and the rinsings are added to the beaker. The extracts from this point on are treated as described above.

B. Chromatography. Previous work (*2*) established the R_f value for cholesterol and cholesterol esters as 0.87 to 0.95 when water-saturated 1-butanol was used as the developing solvent and ascending chromatography was employed. From 6 to 300 micrograms of cholesterol can be successfully chromatographed.

The paper strips (Whatman No. 1, 2.5 × 20 cm.) are developed with the solvent at room temperature (27° C.). The optimal time for development is 10 hours; however, development for from 8 to 12 hours also yields satisfactory results. A blank strip, to which solvent only is applied, is run simultaneously, as well as a "tracer" strip with a known quantity of cholesterol.

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Following development the strips are removed, and the position of the cholesterol on the tracer strip is checked by dipping the strip into Liebermann-Burchard reagent. Portions of the test strips bearing the cholesterol are then cut out, carefully folded, dropped into the micro-Soxhlets, and extracted with chloroform for 0.75 hour on a steam bath.

The cooled extracts are transferred to Evelyn colorimeter tubes immersed in a 50° C. water bath and evaporated to dryness, using the vacuum manifold mentioned above.

C. Colorimetry. Ten milliliters of chloroform are added to each of the colorimeter tubes. The tubes are equilibrated in a 25° C. water bath for 5 minutes, then 4 ml. of the Liebermann-Burchard reagent are added rapidly from a buret with thorough shaking. The tubes are kept at 25° C. in the dark and after exactly 20 minutes are read at 620 mμ in the Evelyn colorimeter.

PRECISION AND RECOVERY

Table I gives data indicating the precision and per cent recovery.

ACKNOWLEDGMENT

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Coulometric Determination of Submicrogram Amounts of Silver

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With the development of sensitive current-measuring devices, coulometry has become an excellent method for the precise determination of very small quantities of an element. A procedure was devised in which amounts of silver ranging from 10^{-8} to 5×10^{-10} gram in 20-μl. to 25-ml. volumes of solution were determined to within approximately 10^{-10} gram by electrodeposition followed by coulometric dissolution of the deposit. The method is capable of detecting and quantitatively estimating quantities of silver at least twenty times smaller than can the best spot test reported by Feigl.

THE quantitative determination of submicrogram amounts of metals has been seriously hampered by the lack of suitable methods. Coulometry, however, is theoretically capable of being applied to such quantities because a millimicrogram of silver, for example, should require 8.94×10^{-7} coulomb in undergoing oxidation or reduction. This corresponds to an average current of about 0.1μa. for 8.9 seconds. Up to the present time, three general types of coulometric determinations have been applied. In the first type, which is employed in the present study, the number of coulombs required to dissolve a substance is measured. Grower (*8*) in 1917 and later Francis (*7*) and Ogarev (*13*) utilized this method to determine the thickness of metal coatings. Campbell and Thomas (*2*) similarly determined the thickness of oxide coatings on metals. Zbinden (*21*), in a procedure later employed by Elema (*4*), determined 10 to 100 micrograms of copper by deposition followed by dissolution. The same procedure was also used by Zakharevskiĭ (*20*) for determining lead and copper.

One can also measure the coulombs required for deposition of an element instead of those for dissolution, as illustrated by the work of Lingane (*10*) and Trishin (*18*). This type of measurement might become less exact as the initial concentration of the ion becomes smaller, because the contribution of the residual current to the total current might assume major proportions.

The third type, coulometric titration, was introduced in 1938 by Szebelledy and Somogyi (*17*), who standardized solutions of hydrochloric and sulfuric acids by neutralization with electrolytically generated hydroxyl ion, the amount of hydroxyl generated being determined by the number of coulombs passed. This technique has been expanded and applied to a variety of determinations (*1*, *3*, *5*, *6*, *11*, *12*, *15*, *16*, *19*).

The method described in the present study is similar to that of Zakharevskiĭ and Zbinden, except that the deposit is dissolved by changing the potential uniformly in a positive direction and measuring the current on an automatic recording potentiometer. When the chart speed is known, integration of the resulting current-time curve gives the number of coulombs, from which the amount of deposit may be calculated. It was felt that the constant current method would be less satisfactory because very small currents would be required and relatively high residual currents might be encountered, which would result in current efficiencies less than 100%.

APPARATUS

Two rapidly interchangeable circuits, one for plating and the other for dissolution, have been incorporated in the instrument shown in Figure 1. Six electrolytic cells can be operated simultaneously and independently and any one of the six can be switched instantaneously into the dissolution circuit without disturbing the other five.

The plating circuit is essentially a voltage divider across a 6-volt storage battery. A reversing switch is provided, so that either positive or negative potentials versus a reference half-cell may be obtained. Similarly, the dissolution circuit consists of a 6-volt battery connected across another voltage divider, whose output, in turn, is applied across a motor-driven slide-wire. This arrangement allows one to select the size of the span (range) of potential to be traversed by the slide-wire. The starting potential can be displaced in either direction by means of a separate 1.5-volt dry cell and its associated voltage divider.

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The current is determined by measuring the potential drop across a precision resistor (Leeds & Northrup, No. 4775 decade resistance box) connected in series with the electrolytic cell using a Leeds & Northrup Speedomax automatic recording potentiometer having a full scale sensitivity of 2.5 mv., a full scale travel time of 1.2 seconds, and a chart speed of 10 inches per minute. When the slide-wire and the chart are both moving, the resulting curve is effectively a current-time curve.

PROCEDURE

Exploratory studies were carried out using 50-ml. portions of 1.00×10^{-5} M silver in 0.1 N acid (either nitric or sulfuric). The 10^{-5} M silver was made up by diluting a standard solution of 1.00×10^{-3} M silver sulfate or silver nitrate (depending upon which acid was used). The standard solutions were prepared from reagent grade chemicals in distilled water and were stored in the dark in black bottles.

Deposition took place on a platinum electrode connected through appropriate salt bridges to a large saturated calomel reference electrode (SCE), used as an anode. After plating for a fixed length of time (measured with a stop watch) from an unstirred solution, the cell was switched instantaneously to the dissolution circuit and the current-time curve was recorded. Integration of the area under the curve was performed with a planimeter.

VARIABLES

The principal variables are the electrode area, the blank due to residual current, the rate of changing the voltage during dissolution, the motion of the solution, the temperature, the time constant of the recorder, and the reproducibility of measuring the area.

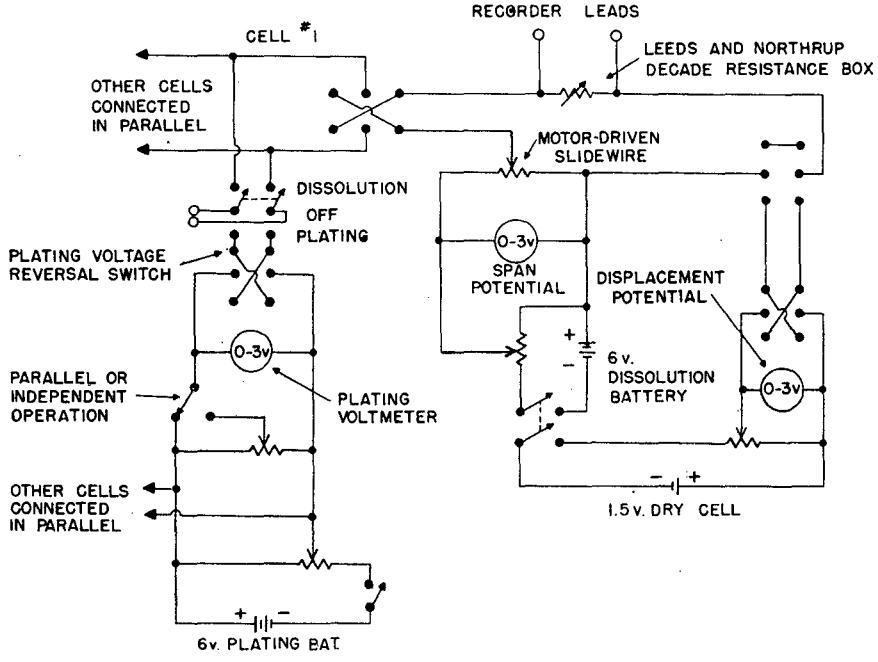

Figure 1. Plating-Dissolution Circuit

Electrode Area. The larger the area of the plating surface, the larger the background due to the generation or removal of gas, usually oxygen or hydrogen, during dissolution, and the larger the amount of silver that will plate out of a particular solution in a given time. Silver was deposited from a 1.00×10^{-5} M silver solution in 0.1 N nitric acid on platinum electrodes whose apparent surface areas varied from 0.002 to 2.0 sq.cm. for exactly 1 minute at a potential of 0.00 volt versus the saturated calomel electrode. Under these conditions, one would expect the ratios of the amount plated to the electrode area as well as the ratio of the residual current to the electrode area to be constant. The data in Table I show this to be only approximately so. While the data show considerable variation, a smaller electrode tends to have both a greater plating rate and a greater residual current in proportion to its apparent area. Also, the ratio of the number of coulombs due to residual current to those due to silver is larger for a small electrode. However, the increase in residual current is proportionately greater than that due to silver. Thus, a lower limit on electrode size is imposed by the relatively large size of the residual current. An electrode size, optimum compromise between plating rate and size of blank, appears to be about 0.2 sq. cm.

Table I. Effect of Electrode Area on Residual Current and Amount of Silver Found at Constant Plating Time

Electrode Area, Sq. Cm.	Rel. Area of Peak	Ag Plated/ Electrode Area	Residual Current/ Electrode Area	Residual Current/ Ag Plated
0.002	0.0086	4.3	37.3	8.7
0.06	0.138	2.3	11.7	5.1
0.16	0.26	1.6	9.9	6.2
0.35	0.61	1.7	10.2	6.2
0.56	1.16	2.1	8.7	4.1
2.00	2.97	1.5	4.5	3.0

Blank Determination. It was necessary in all cases to subtract the residual current from the curve obtained with silver, as might be expected (Figure 2). Experience has shown that a suitable blank can be determined most accurately by plating for the same length of time from a similar solution having no silver. It is unfortunate that such a correction is necessary, because it constitutes an element of uncertainty, particularly at high sensitivities where the background is not linear.

Rate of Change of Potential during Dissolution. The effect of the rate of change of potential during dissolution was evaluated by plating from a 10^{-5} M silver solution onto a 0.5 sq. cm. electrode for 1 minute and then adjusting the speed of the motor-driven slide-wire to different rates. The range covered during a sweep was from 0.00 volt (the potential at which plating was done) to +1.00 volt. *vs.* S.C.E. As the area due to current flow during dissolution theoretically remains constant regardless of polarization rate, it is obvious that the upper limit on the rate is determined by the speed of response of the instrument, and the lower limit by the accuracy with which one can measure the area of a curve having a low peak and a long base, the latter being corrected by a substantial blank. The optimum range as shown in Figure 3 appears to be between 0.04 and 0.06 volt per second.

Movement of Solution. Any motion of the solution will result in an increased plating rate over that obtained in a stationary solution. Attempts to control agitation arising from vibration met with only limited success. Current-time curves made with a stationary platinum electrode showed a variation of ±4% in area for a plating time of 3 minutes in a 10^{-3} M solution. The error due to vibration should be decreased by using an electrode rotated at a rapid, constant rate (*9*), or eliminated entirely by carrying the deposition to completion before dissolving the deposit.

Planimeter Errors. The planimeter used in this study was designed to measure areas up to 10 to ±0.01 sq. inch. The alternative method of cutting out the curves and weighing the paper was discarded because it seemed undesirable, particularly in the preliminary work, to take the chance of destroying a result by making an erroneous correction for the residual current.

By using triangles of several different sizes with known areas, it was found that the reproducibility and accuracy depended to a large extent on the skill of the operator. The precision of successive readings was greater for equilateral triangles than with those whose height was several times greater than the base. The ratios of the area to the distance traveled by the planimeter (the circumference) should be kept as large as possible. The area of figures whose height was approximately twice the base (roughly the dimensions of the curves actually encountered) could be determined to ±0.01 sq. inch.

Recorder. With a chart speed of 10 inches per minute and a pen travel time of about a second to cross the chart, a sizable error would be introduced if the current changed rapidly during dissolution. During exploratory runs it was found that the current increased and decreased relatively slowly, provided that the rate of change of voltage was not too rapid. Hence, the error introduced by the recorder appeared to be negligible.

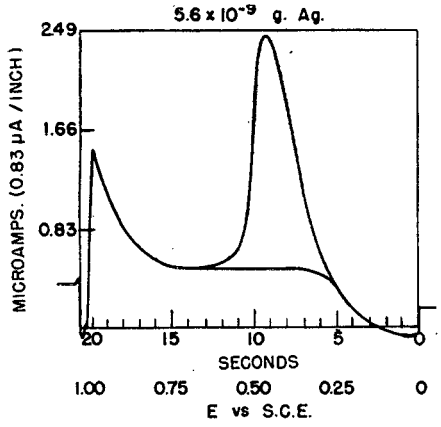

Figure 2. Coulometric Dissolution Curve for Silver

Temperature. It is known from polarography that the diffusion coefficient alone increases 2 to 5% per ° C. (*9*), so that it was highly desirable to carry out all depositions at approximately the same temperature. The fluctuations in room temperature were never more than ±0.2° C. during a given set of determinations. The temperature effect, of course, would be of minor importance if plating were carried to completion.

DETERMINATIONS IN MICROLITER VOLUMES

Determinations of silver ranging in amounts from 2.5×10^{-8} to 2.5×10^{-10} gram in 20 μl. of solution were carried out in specially constructed cells (Figure 4).

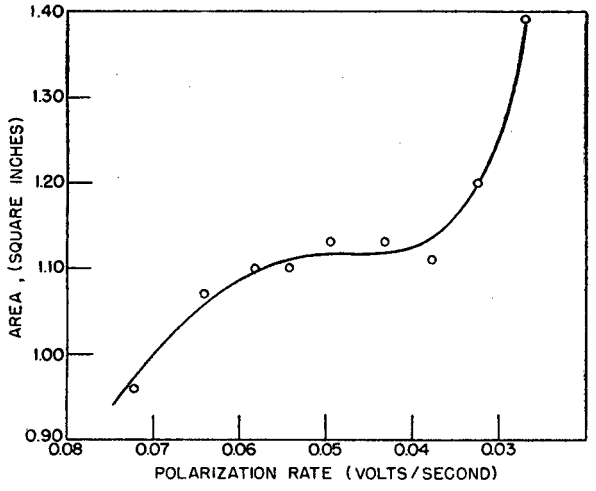

Figure 3. Effect of Rate of Change of Potential during Dissolution on Area of Current-Time Curves

The cathode consists of a 1 sq. cm. piece of platinum foil, to which a copper wire is fused. The foil is embedded in beeswax in a 1 × 1 × 0.75 inch polystyrene box, keeping a fixed area of the foil uncovered to act as the active plating surface by placing a lightly greased No. 1 cork borer against the center of the foil while the wax is poured. The technique of waxing the entire surface and then scraping away some of the wax to expose an active surface proved unsatisfactory. The copper wire is coiled to absorb vibrations which might loosen the coating of wax when the cell is being connected into the circuit. Protection against evaporation is afforded by covering the box and by placing a few drops of water in depressions in the wax on either side of the foil.

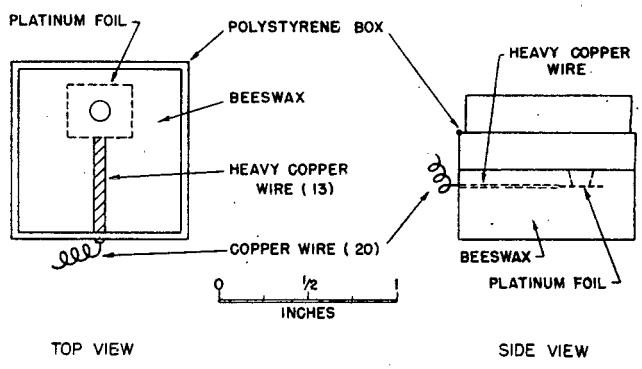

Figure 4. Electrolysis Cell for Microliter Volumes of Solution

The salt bridge and reference cell shown in Figure 5 consist of an agar-filled capillary tip joined by a saturated aqueous potassium sulfate solution to another agar tube, which dips into a connecting solution of potassium sulfate. An agar bridge saturated with potassium chloride forms the final link to the saturated calomel electrode. The sulfate solution between the tip and the rest of the bridge allows for day-to-day expansion and contraction of the system without pushing the agar out of the tip.

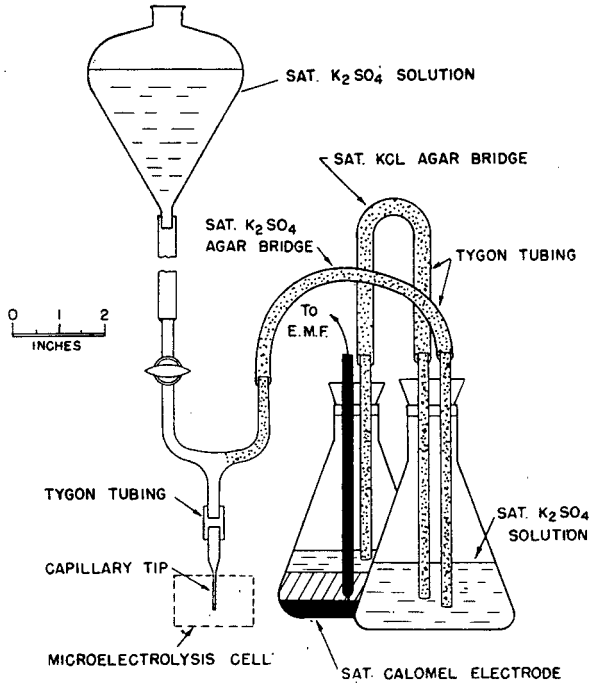

Figure 5. Standard Cell and Salt Bridge for Use with Microelectrolysis Cell

Excess solution is held in a reservoir which is open to atmospheric pr ssure. In operation, the sample is placed in the exposed foil and the capillary tip of the salt bridge is introduced into the drop through a hole in the cell cover. When the salt bridge is not in use, the tip is kept immersed in a saturated solution of potassium sulfate to prevent the agar from drying out.

The solutions were measured out by means of a 10-μl. micro-

pipet in conjunction with a Clay-Adams 1-ml. pipetter. Pipetting was improved by grinding the tip down to a point and thinly coating it on the outside with silicone stopcock grease, thereby reducing the size of the drop that adheres to the tip. After the solution in the pipet has been brought to the mark, excess liquid on the tip can be removed easily without withdrawing any liquid from inside the pipet by quickly brushing the tip at an angle of about 45° against a piece of filter paper.

When a newly constructed cell is first placed in operation, the background is excessively high. Reduction of the background can best be accomplished by making three or four depositions to "condition" the surface. The background was lower for sulfuric than for freshly boiled nitric acid of the same concentration; therefore, sulfuric acid was used in most of these studies.

Per Cent Deposited *vs.* Time. In order to determine the length of time required to deposit silver completely, several runs were made on samples consisting of 10 μl. of 10^{-5} M silver followed by 10 μl. of 0.1 N sulfuric acid wash solution. The electrode was held at a potential of 0.00 volt *vs.* SCE at a temperature of 28° C., and the dissolution operation covered the range from 0.00 to +1.00 volt *vs.* SCE at a rate of 0.05 volt per second. The results (Figure 6) show that essentially all the silver was removed from the solution after 1 hour, but the areas indicate that only about 80% of the theoretical amount of silver was accounted for even after 1.5 hours of plating. This value corresponds to a current efficiency greater than 100%—i.e., mechanical stripping. These electrodes were found to exhibit this behavior with concentrations of silver as great as 10^{-3} M.

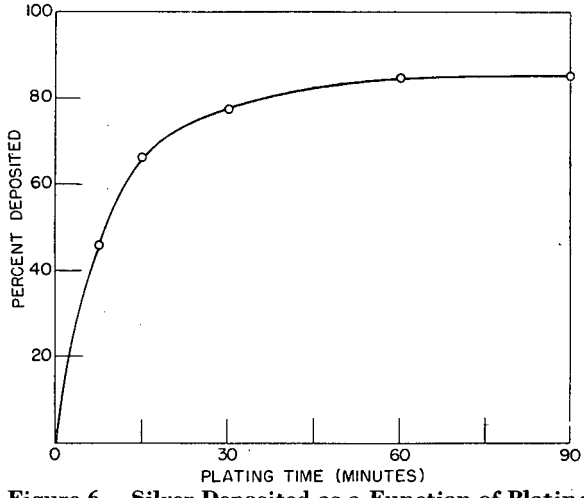

Figure 6. Silver Deposited as a Function of Plating Time

Reproducibility. To determine the reproducibility of the results, five runs were made with each of several different electrodes over a period of a week. In each case, a 10-μl. sample of 1.00×10^{-5} M silver was electrolyzed for 45 minutes and redissolved as described above. The results in Table II show that the average areas for the dissolution curves obtained with different electrodes were different. The theoretical area obtainable from 1.00×10^{-10} mole of silver is 1.93 sq. inches at a recorder sensitivity of 0.833 μa. per inch deflection, while the average actually obtained was 1.42 sq. inches. This indicates that the current efficiency, while reproducible, was greater than 100% and varied slightly from electrode to electrode. It was also noted that the current efficiency of a particular electrode increased gradually with usage, on the order of 5% for 30 cycles of plating and dissolution. The normalized average deviation of areas of the dissolution curves for all the electrodes was 2.3%, corresponding to ±0.033 sq. inch.

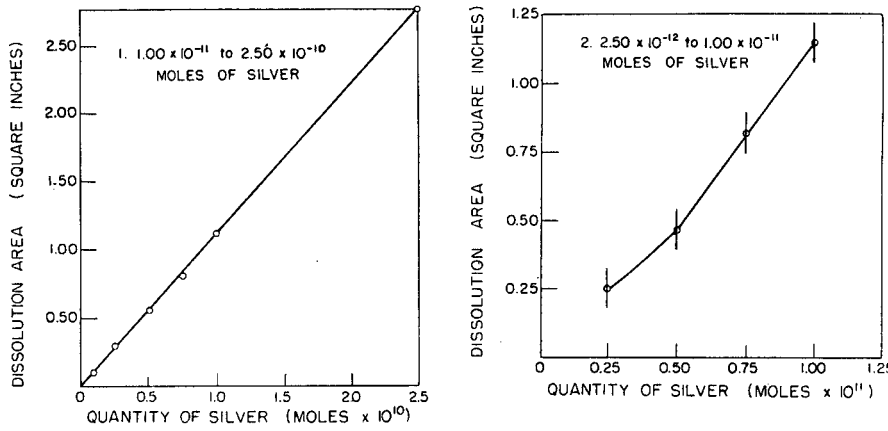

Figure 7. Calibration Curves Using Microliter Volumes of Solution
1. 1.00×10^{-11} to 2.50×10^{-10} mole of silver
2. 2.50×10^{-12} to 1.00×10^{-11} mole of silver

Calibration Curves. Calibration curves were prepared for quantities of silver ranging from 2.50×10^{-12} to 2.50×10^{-10} mole of silver in 20 μl. of 0.1 N sulfuric acid (1.25×10^{-1} to 1.25×10^{-1} M). Because of the necessity of keeping the recorder pen on the chart at all times, the curves were broken into two ranges, one from 2.50×10^{-12} to 1.00×10^{-11} mole, and the other from 1.00×10^{-11} to 2.50×10^{-10} mole. The sensitivity of the recorder in the former case was set to 0.0833 μa. per inch deflection, and in the latter case to 0.833 μa. per inch. Figure 7 shows the calibration curves for the two ranges. In the upper range, the relationship is linear and passes through the origin. In the lower range, the relationship is linear down to 5×10^{-12} mole of silver, but the curve does not pass through the origin. This phenomenon may be due to inability to correct adequately for the blank when the background-to-peak ratio is large or to the delayed dissolution of the layer of silver atoms in direct contact with the platinum surface. Both factors are discussed in more detail in the following section. The variations in the measured areas are considerably larger in this region ±0.08 sq. in.

Other Studies. The above technique has also been applied to 10-μl. volumes using a 5-μl. sample and 5 μl. of sulfuric acid. the results, however, are not as satisfactory because of increased difficulty in working with smaller volumes.

Table II. Reproducibility of Dissolution Areas Obtained by Dissolving Silver Deposited from 20 μl. of Solution Containing 1.00×10^{-10} Mole of Silver

Electrode 1		Electrode 2		Electrode 3		Electrode 4		Electrode 5		Electrode 6	
Area, sq. inch	Dev.	Area, sq. inch	Dev.	Area, sq. inch	Dev.	Area, sq. inch	Dev.	Area, sq. inch	Dev.	Area, sq. inch	Dev.
1.43	0.026	1.41	0.022	1.40	0.42	1.50	0.022	1.30	0.046	1.48	0.056
1.50	0.044	1.44	0.008	1.36	0.002	1.54	0.018	1.26	0.086	1.40	0.024
1.47	0.014	1.41	0.022	1.37	0.012	1.54	0.018	1.38	0.034	1.44	0.016
1.48	0.024	1.46	0.028	1.30	0.058	1.53	0.008	1.42	0.074	1.35	0.074
1.40	0.056	1.44	0.008	...	...	1.50	0.022	1.37	0.024	1.45	0.026
Av.											
1.456	0.033	1.432	0.018	1.358	0.028	1.522	0.018	1.346	0.053	1.424	0.039

Normalized av. 1.419 ± 0.032 sq. inches.

Studies have also been made of the deposition and dissolution of cadmium from micro volumes of solution using mercury electrodes. The results to date look very promising.

DETERMINATIONS IN LARGE VOLUMES

In working with large volumes (25 ml.) of very dilute solutions, deposition onto a stationary microelectrode would not only be very time-consuming but also inaccurate, owing to variations arising from any irregular motion of the electrode or the solution. Accordingly, these studies were performed using a microelectrode rotated at a constant speed of 600 r.p.m. by means of a synchronous motor which, from polarography, is known to result in faster and more reproducible deposition.

In these experiments, the silver was contained in 25-ml. portions of 0.1 N potassium sulfate. Sulfuric acid was found to be unsuitable as a supporting electrolyte because hydrogen evolved during deposition of the silver resulted in a second dissolution peak which overlapped that for silver. As extreme dilutions of silver were used, it was necessary to remove all possible contaminants by doubly distilling the water and pre-electrolyzing solutions of potassium sulfate using a mercury cathode. The deposition and dissolution were carried out in the manner described previously. In order to deposit silver from very dilute solutions, a potential of −0.1 volt *vs.* S.C.E. was required, so oxygen was removed before deposition by bubbling prepurified nitrogen through the samples.

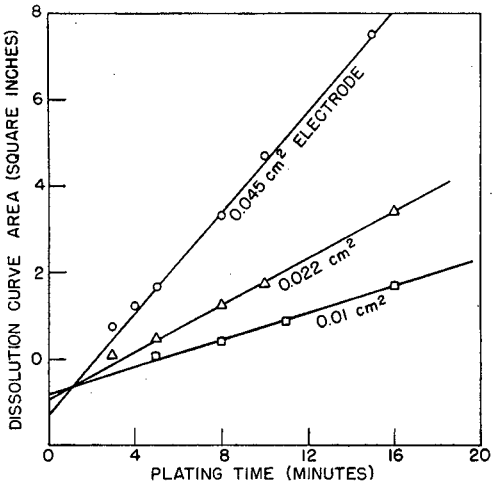

Figure 8. Dissolution Area *vs.* Plating Time for Rotating Platinum Microelectrode

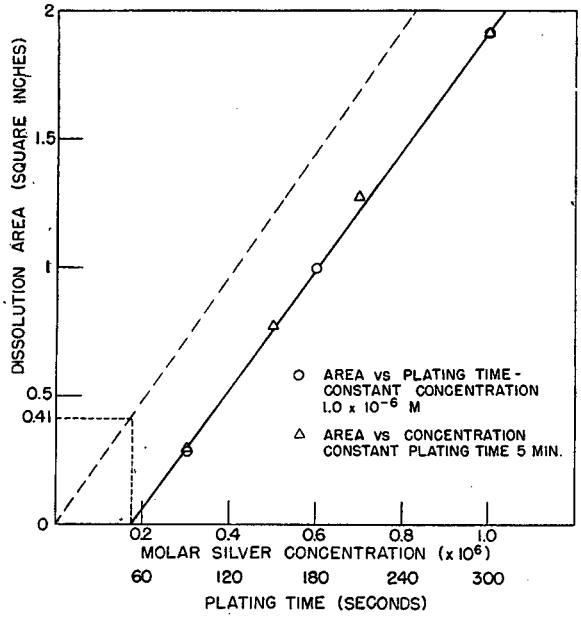

Figure 9. Calibration Curve for Rotating Microelectrode

Variation of Dissolution Area with Time of Deposition and Area of Electrode. For a given electrode, the variation in the quantity of silver deposited, as measured by the dissolution area, is linear with the plating time, as shown in Figure 8. In going from one electrode to another, the slope of the line increases with increasing electrode area. Contrary to what one might ordinarily expect, the lines intersect below and to the right of the origin. The fact that the intersection point lies to the right of the origin is probably due to the failure to dissolve the first layer of silver atoms deposited onto the platinum in the same region of potential as the rest. It has been shown (*14*) that a considerably more positive potential is required to dissolve this layer than to dissolve those deposited onto silver. The fact that the lines intersect at a point below zero indicates that although the best blank possible has been used, an overcorrection has been made.

Variation of Dissolution Area with Concentration of Silver. Figure 9 shows a linear relationship between concentration and dissolution area for a particular electrode (3 mm. long) in the range from 2×10^{-7} M to 10^{-6} M silver at a constant plating time of 5 minutes at a potential of −0.10 volt *vs.* SCE. This figure confirms the expectation that changes in plating time have exactly the same effect as corresponding changes of concentration. The curve has a reproducible translation corresponding to 0.41 sq. inch. By extending the plating time to 30 minutes, a similar calibration curve can be obtained with concentrations as low as 5×10^{-8} M. By extending the plating time even further, correspondingly lower concentrations should be measurable.

In general, the technique appears to be useful because it can be both qualitative and quantitative. By control of the cathode potential, one can select an element to be deposited; by measuring the coulombs during dissolution using an integration procedure, one can determine millimicrogram amounts or submicromolar concentrations of an element.

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NOTES ON ANALYTICAL PROCEDURES . . .

Capacitor Cell Modification of Chemical Oscillometer

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ATTEMPTS to apply the heterodyne type of chemical oscillometer developed by West, Burkhalter, and Broussard (*4*) to industrial analysis of systems of nonelectrolytes led to an increased demand for additional sensitivity and suggested the desirability of a smaller sample size. The volume of sample required by the original instrument (20 ml.) was rather large when the amount of sample was limited or continuous sampling of a reaction product was desired. Substitution of a capacitor cell for the coil type of cell involved problems of circuit design which are not immediately obvious and which indicated applications that were not previously possible.

The stability of instruments of this type is largely dependent on the "figure of merit" or Q of the components of the circuit; Q is the ratio of reactance to radio-frequency resistance. Good practice in electronics engineering (*3*) requires that the diameter of the coil used in the tank circuit be large compared to the height of the coil. Ordinarily, the coil should be wound with wire having the maximum surface consistent with the available space and the individual turns should be spaced with a separation approximately equal to the diameter of the wire. These requirements suggest that the optimum coil for the frequency employed in these instruments (about 5 megacycles) should have a diameter of approximately 4 inches (10 cm.) and a height of about 2 inches, wound with wire of about gage 8. An inductor of this size requires a sample of about 200 ml. The difficulty imposed by increased sample size may be avoided by constructing a cell in which the sample is contained between concentric walls and confined to the region immediately inside the coil form. By this device, the sample may be decreased by a factor of 2 to 5 with approximately 80% of the effectiveness of a sample filling the whole interior of the inductor, but the cells are somewhat difficult to reproduce and channeling or holdup of flowing samples may lead to erroneous results.

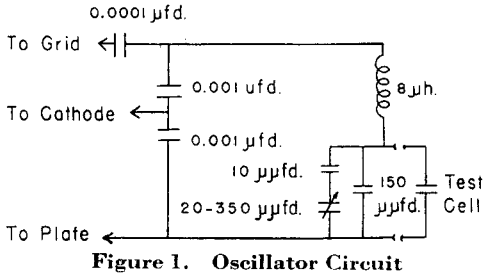

Figure 1. Oscillator Circuit

The requirements for a capacitor, on the other hand, are only that a high dielectric be maintained between the plates of the condenser and that the capacitance may be increased, for a given plate area, by decreasing the spacing between the plates. While the first requirement is beyond the control of the designer, because the dielectric material is the sample being studied, the second requirement is precisely the one desired if the sample size is to be decreased. By a suitable design of the plates and the shape of the entrance chambers, channeling and sample holdup may be controlled.

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The cells used were constructed in the glass-blowing shop by flattening a section of large-diameter glass tubing and attaching 8-ml. tubing to the two ends of the cell. The over-all shape of the cell is that of a disk. Sheet metal plates were then attached to the two flat surfaces of the cell with polystyrene cement and the electrical connections were made firm by wrapping the leads and input tubes with wire. The capacitance of the cells varied between 5 and 8 micromicrofarads.

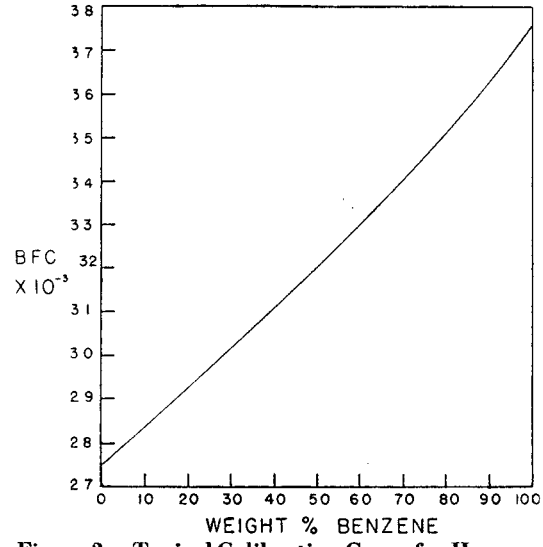

Figure 2. Typical Calibration Curve for Hexane-Benzene Mixture

In order to attain the maximum frequency change for a given material, it was necessary to change the L/C ratio and the size of the capacitors used in the oscillator, to make the capacitance of the cell as large a fraction as possible of the total capacitance of the frequency-determining circuit. The capacitance of the cell having been fixed by its physical dimensions, satisfactory performance could be attained only by careful circuit design. The best sensitivity attained with satisfactory stability required that the oscillator operate very near the "overload" point at which the power drawn by the tank circuit was sufficient to stop the oscillations. The actual point of operation chosen depended on the range of dielectric constants encountered in the samples investigated. In the model discussed here, formamide and pyridine caused the oscillations to cease. The modified portions of the tank circuit are illustrated in Figure 1; the complete circuit has been published (*4*).

A number of samples studied previously with the "coil cell" model were reinvestigated with the modified instrument. In all cases, a marked improvement was noted; the greatest improvement was in the frequency changes produced by materials that had formerly changed the frequency of the working oscillator by 1000 cycles or less and now produce changes that are greater by factors up to 40. Materials of higher dielectric gave less markedly improved results, but the factors were still of the order of 15 or more.

The frequency differences were measured by supplying the output of the oscillometer to the vertical input of an oscilloscope and

the output of a Hewlitt-Packard oscillator, Model 200 C, to the horizontal input. The circular Lissajous figure was used to determine the equivalence point. The stability and drift of the new instrument were approximately the same as those of the previous model (*4*), although it was difficult to make exact measurements because of the wide range of frequency covered and the lack of test equipment of sufficient precision to guarantee that the observed drifts arose in the instrument discussed here and not in the comparison oscillator. The reproducibility of the measurements was within the calibration of the comparison oscillator. The data reported in this paper imply that, for an average of three measurements, beat frequency change values are accurate to within 50 cycles. The signal generator dial could not be read more accurately nor was its stability reliable within closer limits.

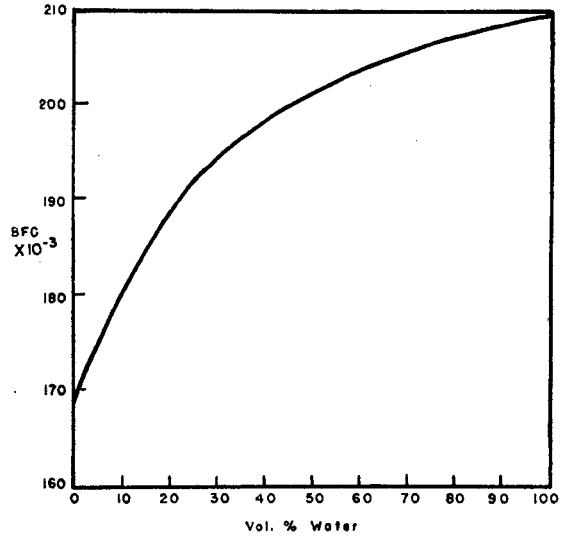

Figure 3. Typical Calibration Curve for Acetone-Water Mixture

The influence of temperature on the frequency of the individual oscillators and on the difference frequency was accentuated by the increase in sensitivity, and more careful temperature control was necessary than that formerly required. The temperature coefficient for both sample and instrument was of the order of 40 cycles per degree centigrade. This temperature control was readily effected by storing the samples in a constant temperature bath for sufficient time to permit them to come to the predetermined operating temperature. Adoption of the instrument on a fairly wide scale and its manufacture would require attention to temperature-compensating components. No attempts have been made in this laboratory to carry the engineering development of the instrument beyond the point required for laboratory use.

The effect of varying sample temperature was noted in the previous instrument, but the extent of the effect in that case is to shift the beat frequencies of all points of an analytical calibration curve but to leave the new curve essentially parallel to the original. In the case of the capacitance cell instrument, the slope of the curve may change appreciably if the temperature is not controlled.

Table I. Beat Frequency Changes

Substance	Beat Frequency Change	
	Coil	Condenser
Water	7880	210,000
Methanol	5560	189,000
Ethyl alcohol	4760	178,000
n-Amyl alcohol	3370	149,000
Acetone	4400	168,500
n-Hexaldehyde	2520	122,000
Methyl isobutyl ketone	3230	146,500
Propionic acid	1240	89,000
Methyl propionate	1890	102,500
Ethyl acetate	1790	100,000
Benzene	810	37,000
Toluene	830	39,500
Bromobenzene	1670	91,500
Nitrobenzene	5720	192,000
Aniline	2040	107,000
n-Heptane	670	27,500
2-Heptene	780	33,000

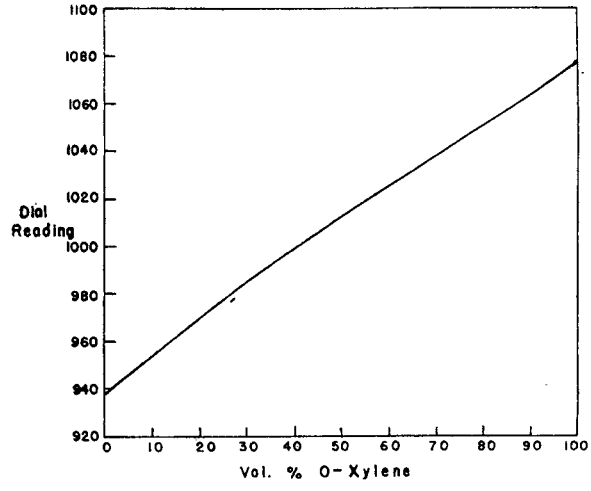

Figure 4. Typical Calibration Curve for *o*-Xylene-*p*-Xylene Mixture

Table I compares the frequency differences observed between the empty cell value and the value when the cell was filled with a sample and measured with the two instruments. The actual values of the beat frequency change are not to be taken as characteristic of the material, except for comparison purpose, because the design of the cell, the circuit employed, and even variation in individual components may cause different values to be observed with different models. In fact, almost any desired degree of sensitivity may be attained by appropriate choice of the relative magnitudes of inductance and capacitance employed, but each change in sensitivity requires that the problem of stability be solved for the circuit values chosen. The order of change is not strictly preserved in the two instruments; the answer to this problem lies in the fundamental physical constants being evaluated. This problem is, at present, under investigation in these laboratories.

Figures 2 and 3 illustrate calibration curves prepared in this laboratory for the analysis of mixtures of hexane in benzene and water in acetone. The curves are sufficiently linear over small ranges of concentration to permit satisfactory interpolation, but it is characteristic of these instruments that the slope of the calibration diagrams may vary widely with concentration and that a method of extreme sensitivity and accuracy may be available for one concentration region of a given mixture while another region may not be satisfactory for analytical purposes.

In order to keep the oscillators operating as nearly as possible at a given frequency at all times, the working oscillator was equipped with a precision dial and measurements were made of the number of dial divisions required to restore the working oscillator to its original frequency after the sample had been introduced into the cell. Figure 4 illustrates the application of this technique to the analysis of a mixture of *o*- and *p*-xylenes. The dial divisions necessary to restore the null balance are plotted against the concentration of *o*-xylene. The linearity of plots of this type depends, in addition to the factors previously mentioned, on the shape of the plates of the variable condenser used to restore the oscillator to its original frequency. The condenser used in this case had plates of the "midline" shape.

Subsequent to the submission of this paper, Blaedel and Malmstedt (*2*) published results obtained with heterodyne instruments.

In their investigations, emphasis was placed on titrations of systems of electrolytes with a capacitor cell. For applications of that type, changing the frequency may have marked effects on the performance of the instruments. The loading of the oscillator, however, precludes the great increases in sensitivity which may be obtained with careful L/C balance and systems of nonelectrolytes. For example, with an instrument of the type used by Burkhalter, West, and Broussard (*4*), the substitution of a capacitor cell for an "inductance" cell may make sample handling more convenient but leads to no appreciable change in sensitivity for solutions of electrolytes. These observations were confirmed by the work of Blaedel and Malmstedt (*2*).

Anderson and Betts have published (*1*) data on studies of systems of electrolytes with an instrument of the "grid-dip" type. This instrument gives excellent results in the hands of the authors in comparison to other similar instruments; there is an important frequency effect.

The heterodyne instruments and, more markedly, those depending primarily on the Q of the circuit are theoretically limited in titrations of electrolytes. For work with electrolytes, the best circuit should be one that does not depend on the detuning of the primary oscillator circuit. The stability required for applications outside of the research laboratory is of the order of 1 part in 10^7, a requirement that is very difficult to achieve even with the highest quality components. Introducing solutions of electrolytes as dielectric materials is in direct opposition to the requirements for stability.

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Identification of Alcohols in Dilute Aqueous Solution

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IN THE course of an investigation of the volatile constituents of fruits, methods were desired for the isolation of derivatives of alcohols from very dilute aqueous solutions and for the fractionation of less than 1 mg. of mixtures of alcohol derivatives. By the use of modified Schotten-Baumann conditions Henstock (*1*) prepared *p*-nitrobenzoates from 0.25 to 1.5% alcohol solutions, Lipscomb and Baker (*3*) prepared 3,5-dinitrobenzoates from 5% alcohol solutions, and White (*7*) prepared 3,5-dinitrobenzoates from 0.5% alcohol solutions. However, none of these workers extended the preparation of derivatives to lower concentrations. By using the procedure of White under controlled conditions 3,5-dinitrobenzoates were obtained from primary alcohols at a concentration of 0.001% (100 micrograms of ethyl 3,5-dinitrobenzoate were obtained from 10 ml. of 0.001% ethyl alcohol; 20% yield). No attempt was made to investigate lower concentrations, as the methods of detection and identification of the 3,5-dinitrobenzoate became limiting.

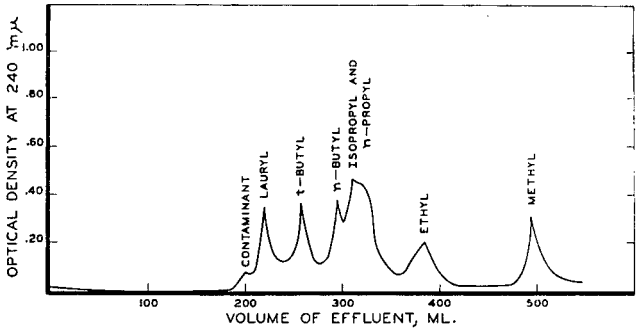

Figure 1. Chromatographic Separation of Mixture of 100 Micrograms of Each of Seven 3,5-Dinitrobenzoates

The excellent chromatographic method described by White and Dryden (*8*) for the separation of 3,5-dinitrobenzoates involves the use of a fluorescent indicator on a silicic acid–diatomaceous earth column. It requires approximately 1 mg. of a 3,5-dinitrobenzoate for detection. In the present work the fluorescent indicator has been omitted. The eluate is collected systematically in fractions, and the concentration of 3,5-dinitrobenzoate in each fraction is estimated spectrophotometrically. This makes possible the detection of as little as 30 micrograms of a 3,5-dinitrobenzoate.

PREPARATION OF 3,5-DINITROBENZOATES

To 10 ml. of the aqueous solution in a 100-ml. glass-stoppered flask are added 0.1 ml. of redistilled pyridine and 1 ml. of benzene (commercial). The mixture is cooled in an ice bath, and 11 grams of anhydrous potassium carbonate are added at such a rate that the temperature does not exceed 25° C. A solution of 0.5 gram of 3,5-dinitrobenzoyl chloride (Eastman) in 2 ml. of benzene is added in portions at room temperature with shaking. Three minutes after the addition of the acid chloride is complete, 30 ml. of sodium-dried ether are added and the mixture is shaken. The ether is decanted into a centrifuge tube. The extraction is repeated twice. The ether solutions are centrifuged, filtered through a dry filter paper, and evaporated at atmospheric pressure. The residue is heated at 70° to 80° at 20 mm. until the odor of pyridine can no longer be detected. The residue is extracted with 10 ml. of hot petroleum ether (ligroin). After cooling, this solution is applied to the chromatographic column.

CHROMATOGRAPHIC SEPARATION

The column is a 1.8 × 40 cm. borosilicate glass tube which is joined at the top to a 100-ml. bulb that serves as a solvent reservoir. The tube is constricted at the bottom and joined to a borosilicate glass stopcock. The adsorbent is supported on a plug of

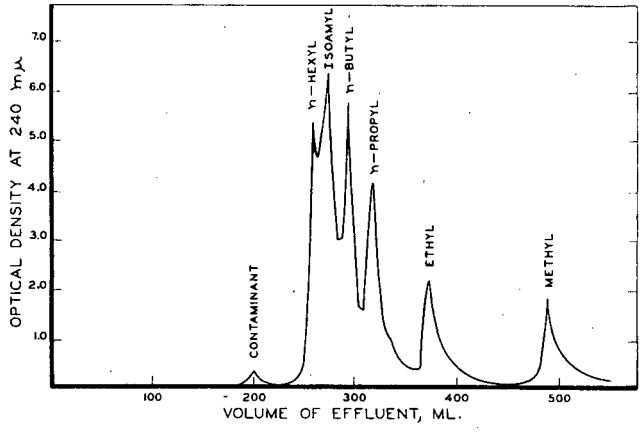

Figure 2. Chromatographic Separation of Mixture of 3,5-Dinitrobenzoates Prepared from Dilute Aqueous Solution of Alcohols

A blank using 10 ml. of water showed that the small peak at 200 ml. is due to a contaminant. It was found in all samples of 3,5-dinitrobenzoates prepared from aqueous solution and showed an absorption maximum at 255 mμ

Table I. Melting Points of 3,5-Dinitrobenzoates Obtained from Chromatographic Separation (Figure 2)

Fraction Effluent Vol., Ml.	Melting Point (Micro. Corr.), ° C.	Reported Melting Point (*2*), ° C.
475–495	105–107	108 (methyl)
360–380	89–92	93 (ethyl)
315–330	67.5–71.5	74 (*n*-propyl)
290–300	63–68	64 (*n*-butyl)
270–280	38–46	61 (isoamyl)
250–260	Not crystalline	59 (*n*-hexyl)

glass wool and a filter paper disk. To avoid contamination, the stopcock is not lubricated. The pressure regulator is described by Marvel and Rands (*4*), and compressed air is used.

The adsorbent is a 2 to 1 (by weight) mixture of silicic acid (Merck, reagent) and Celite analytical filter-aid (Johns-Manville).

The petroleum ether (ligroin) is practical grade (Eastman No. P 513), specially purified to remove impurities that absorb in the ultraviolet. In a typical purification, 2 kg. of petroleum ether are first washed with 500 ml. of concentrated sulfuric acid in a separatory funnel, and then stirred overnight with 3 pounds of fuming sulfuric acid. (The fuming sulfuric acid is added slowly as heat is evolved.) After washing with water and sodium carbonate, the petroleum ether is dried over calcium chloride and distilled. The fraction boiling at 65° to 85° is used. It does not absorb light in a 1-cm. cell in the ultraviolet above 228 mμ. In the recovery of petroleum ether from the chromatographic separation a similar procedure is followed, but the fuming sulfuric acid treatment is omitted.

Eighteen grams of the adsorbent are added all at once to the column without suction, with the stopcock open. The column is gently shaken, and pressure is applied (40 cm. of mercury). The pressure is released gradually. The top of the column is lightly tamped. Fifty milliliters of petroleum ether are added to the column and forced through under approximately 50-cm. pressure. When solvent comes through at the bottom of the column the petroleum ether solution of 3,5-dinitrobenzoates is added. When all this solution has been forced into the column, the developer is added. The eluate is collected in 5-ml. fractions from this point. The developer is forced through under approximately 50-cm. pressure, and flows at the rate of about 1.5 ml. per minute. The following solutions are used:

Vol., Ml.	Petroleum Ether, % (v./v.)	Ether, % (v./v.)
50	100	1
50	99	1
50	98	2
50	97	3
50	96	4
200	95	5
100	90	10

Fresh developer is added when approximately 5 ml. of the previous solution remain above the adsorbent. The use of a developer of gradually increasing ether content resulted in better separation than use of 5% ether throughout.

The optical density of the solutions is read at 240 mμ using a Beckman Model DU quartz spectrophotometer. The solutions were diluted to give optical density readings below 0.70. Ethyl 3,5-dinitrobenzoate shows increasing absorption from 300 to 228 mμ. The wave length 240 mμ is a compromise between convenience and high extinction coefficient (ϵ = 18,000). Beer's law is followed satisfactorily.

RESULTS AND DISCUSSION

Although the preparation of the fluorescent adsorbent and the use of ultraviolet light (*8*) are obviated, by the modifications of the chromatographic method, specially purified petroleum ether is necessary, and the collection of a large number of fractions is tedious unless an automatic fraction collector is available. However, the substitution of the spectrophotometric method of detection of 3,5-dinitrobenzoates for the visual method renders the chromatographic method more sensitive. Figure 1 shows the separation of a mixture containing 100 micrograms of each of seven 3,5-dinitrobenzoates.

By the use of this sensitive chromatographic technique in conjunction with the procedure for preparing 3,5-dinitrobenzoates from dilute aqueous solutions, the detection of alcohols in dilute aqueous solution is made very simple. Figure 2 shows the chromatographic separation of the mixture of 3,5-dinitrobenzoates obtained from 10 ml. of a solution which was 1×10^{-3} *M* in each of six primary alcohols. By evaporation of the solvent from the appropriate fractions, four of the 3,5-dinitrobenzoates were obtained with fairly sharp melting points, as shown in Table I. Further fractionation would be necessary for the isolation of pure material in the case of the other two.

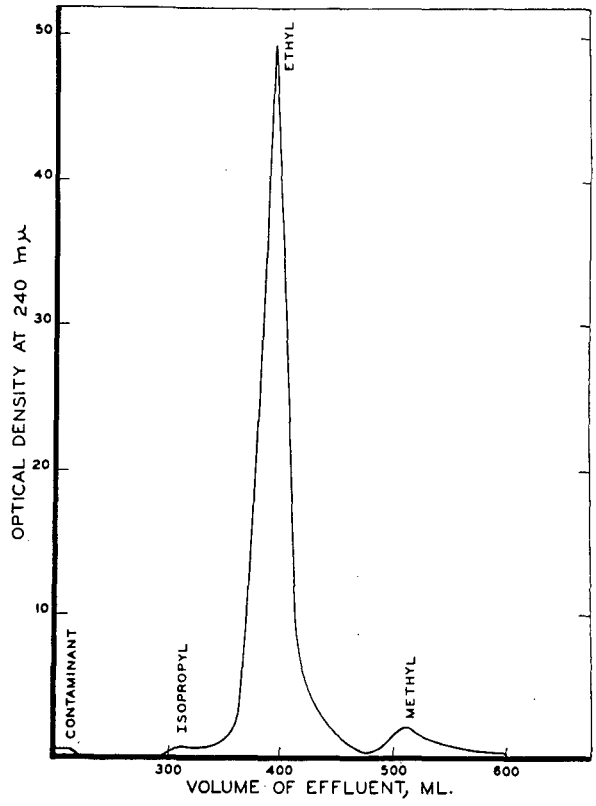

Figure 3. Chromatographic Separation of Mixture of 3,5-Dinitrobenzoates from Grape Juice Fraction

Primary alcohols react more readily than secondary alcohols, which react more readily than tertiary alcohols. A primary alcohol can be detected by this method in solutions as dilute as 1 to 2 $\times 10^{-4}$ *M*. Isopropyl and *sec*-butyl alcohols were detected at a concentration of 1×10^{-3} *M*. A concentration of 0.1 *M* of *tert*-butyl alcohol (0.7%) was necessary for detection.

Esters do not react appreciably under these conditions. A 0.1 *M* solution of absolute ethyl acetate yielded less ethyl 3,5-dinitrobenzoate than did a 2×10^{-4} *M* ethyl alcohol solution, indicating less than 0.2% transesterification.

In their study of chromatography on silicic acid–Celite, Trueblood and Malmberg (*6*) found linear adsorption isotherms for a variety of compounds. They found that the behavior of mixtures was the sum of the separate behaviors of the individual compounds. In the present study, over the range of 100 micrograms to 20 mg. of 3,5-dinitrobenzoate, concentration or the presence of other 3,5-dinitrobenzoates had no apparent effect on the "peak effluent volume" (*4*). The position and shape of the peaks therefore furnish information as to the identity and homogeneity of the fractions, and a judicious selection of material for further study is possible.

The sensitivity of the spectrophotometric determination and the constancy of behavior of compounds in mixtures makes possible the detection of a trace of one 3,5-dinitrobenzoate in the presence of a large excess of another. The fractionation of such a mixture is shown in Figure 3.

Twenty-four milligrams of the mixture were subjected to the chromatographic adsorption. Fraction 350-450 ml. was ethyl 3,5-dinitrobenzoate (20 mg.); fraction 495–525 ml. was methyl

3,5-dinitrobenzoate (1.2 mg.); fraction 300–320 ml. was chiefly isopropyl 3,5-dinitrobenzoate (0.1 mg.). The position of methyl 3,5-dinitrobenzoate is different from that in Figures 1 and 2, as a somewhat different solvent system was used in the development.

The method of separation described here has certain advantages over the paper-chromatographic method of Rice, Keller, and Kirchner (*5*) in that complex mixtures can be separated in a single system, the compounds can be recovered for further study, and somewhat smaller quantities of the compounds are used.

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Estimation of Thorium by Selenious Acid

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THE use of selenious acid to precipitate thorium from neutral or buffered solutions was first reported by Kota (*2*); the thorium selenite was determined gravimetrically. Available information in the literature about the operative conditions and the accuracy and reproducibility of the above method is, however, meager. Series of experiments were, therefore, carried out to investigate the adaptability of selenious acid for quantitative estimation of thorium. The present paper reports a simple iodometric method for its determination in thorium selenite.

EXPERIMENTAL

Pure selenious acid, obtained by recrystallizing a sample of Merck's reagent grade several times from absolute alcohol, was dissolved in water and allowed to stand for about 4 hours. The clear aqueous solution was used to precipitate thorium. Preliminary experiments showed that the precipitation of thorium from its aqueous solution by selenious acid is not quantitative, presumably because of the partial dissolution or hydrolysis of thorium selenite. To an aliquot quantity of pure thorium nitrate (or chloride) solution with a pH adjusted between 5.5 and 6.0, an equal volume of alcohol was therefore added and thorium selenite was precipitated completely by adding a slow stream of an aqueous 20% solution of selenious acid with constant stirring. The precipitate was filtered through Whatman No. 41 paper and washed with 25 to 30 ml. of 2% selenious acid solution followed by absolute alcohol till free from excess of the precipitant. It was then dissolved in a minimum quantity of concentrated hydrochloric acid and diluted to 250 ml. The total acidity of the made up solution was maintained between 1 and 2 *N*.

Table I. Estimation of Thorium by Selenious Acid

Expt. No.	CeO_2 in $CeCl_3$ or $Ce(NO_3)_3$ Added, Gram	ThO_2 Taken, Gram	ThO_2 Obtained, Gram	Difference, Gram
1	...	0.0640	0.0638	−0.0002
2	...	0.0796	0.0798	−0.0002
3	...	0.1558	0.1556	−0.0002
4	...	0.1580	0.1580	...
5	...	0.1014	0.1010	−0.0004
6	...	0.3150	0.3155	−0.0005
7	...	0.2370	0.2350	−0.0020
8	...	0.4740	0.4736	−0.0004
9	...	0.1014	0.1012	−0.0002
10	0.1048	0.1010	0.1008	−0.0002
11	0.1222	0.1558	0.1556	−0.0002
12	0.0766	0.1664	0.1663	−0.0001
13	0.1476	0.2012	0.2014	+0.0002
14	0.1568	0.2136	0.2133	−0.0003

To 10 ml. of this solution about 2 grams of potassium iodide were added and the liberated iodine was titrated against standard thiosulfate (*4*).

Alternatively, the estimation was carried out by adding to a known volume of thorium selenite solution a slight excess of standard thiosulfate and back-titrating it against iodine solution of known strength (*3*). As the addition of a large excess of thiosulfate leads to high results in the iodometric estimation of selenium (*1*), it was necessary to predetermine by trial experiments the appropriate quantity of thiosulfate reacting with the thorium selenite solution taken for titration.

The reaction may be represented as follows:

$$H_2SeO_3 + 4Na_2S_2O_3 + 4HCl \longrightarrow Na_2SeS_4O_6 + Na_2S_4O_6 + 4NaCl + 3H_2O \quad (1)$$

According to Equation 1, 1 mole of selenious acid corresponds to 4 moles of thiosulfate; it follows that a knowledge of the amount of thiosulfate reacting with selenious acid available from thorium selenite serves as a direct measure for the estimation of thorium.

A typical set of results obtained by the alternative method is given in Table I.

In all but one case (experiment 7) the error does not exceed 1%, an accuracy that compares favorably with the classical gravimetric procedures.

Selenious acid precipitates quadrivalent cerium from neutral or slightly acid solutions. Prior reduction of cerium to the cerous condition is therefore necessary to prevent its interference in the estimation of thorium. The addition of excess alcohol to a cerous salt solution leads to the precipitation of cerous selenite. A quantitative separation of thorium from a solution containing cerous salts is therefore carried out by effecting the initial precipitation of thorium selenite in a medium containing not more than 50% alcohol and filtering the precipitate quickly through Whatman No. 41 filter paper. Experiments 10 to 14 (Table I) refer to such a separation of thorium from solutions containing varying quantities of cerous chloride (or nitrate).

ACKNOWLEDGMENT

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Improvement in Anthrone Method for Determination of Carbohydrates

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THE use of anthrone as a qualitative (*1*) and quantitative (*4, 5*) reagent for the determination of carbohydrates has been considerably impeded by the darkening with time of the anthrone reagent, which is usually 0.1 to 0.2% anthrone in 95% sulfuric acid (*2*). The darkening of the reagent has been shown to be inversely related to the purity of the sulfuric acid employed. When the reagent is used quantitatively, this darkening phenomenon creates a need either for careful standarization with respect to the age of the reagent used or for preparation of a new standard curve for each set of carbohydrate determinations.

A modification of Morris' method (*4*) has been devised which avoids the necessity of dissolving the anthrone in sulfuric acid prior to the determination, thus eliminating color variations arising from this source and allowing a single standardization curve to suffice.

To 2 ml. of the carbohydrate solution (containing an amount of carbohydrate that will give a color intensity in the range given by 0 and 80 micrograms of glucose) in a 19 × 150 mm. test tube is added 0.5 ml. of a solution of 2% anthrone (recrystallized from benzene and light petroleum ether) in reagent grade or C.P. ethyl acetate. Then 5 ml. of concentrated sulfuric acid are carefully layered into the tube. The tube is gently swirled until the ethyl acetate has hydrolyzed, as indicated by the floc of anthrone which appears. More rapid swirling then thoroughly mixes the contents of the tube and dissolves the anthrone. The developed color may be read after 10 minutes at 620 mμ in a spectrophotometer against distilled water and corrected for the absorption of a blank containing only the reagents and water.

A plot of the optical density against weight of glucose in the sample gives a straight-line relationship from 0 to 80 micrograms. The acetic acid and ethyl alcohol produced by the hydrolysis of the ethyl acetate do not interfere with the reaction in any way. The ethyl acetate solution of anthrone will keep several weeks when stored in an amber glass-stoppered bottle. Thus, the troublesome development of color in the sulfuric acid–anthrone reagent employed in earlier procedures is avoided.

Using the values reported by Morris (*4*) as conversion factors, a single standard curve prepared from glucose will suffice for the quantitative determination of all carbohydrates listed. By determining the conversion factors, many other hexoses and hexose-yielding compounds, including those listed by Dreywood (*1*), Viles and Silverman (*5*), and Kowald and McCormack (*3*), can be quantitatively estimated in terms of glucose.

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Errors in Volumetric Analysis Arising from Adsorption

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CONWAY (*1*) in his study of errors in volumetric analysis made no mention of adsorption as a possible source of error. However, the importance of adsorption in one analytical method was strikingly demonstrated by Schoonover's (*6*) studies of a colorimetric method for the determination of silver. Furthermore, radiochemists have long been aware of the fact that considerable losses may occur when very dilute solutions are stored in glass containers. A general study of the adsorption of certain ions onto soft glass, borosilicate glass, and metallic surfaces, carried out by Hensley, Long, and Willard (*5*), indicated that it was necessary, for work being done in this laboratory, to determine the magnitude of the losses to be expected from adsorption in pipeting very dilute solutions of silver perchlorate in 0.1 *N* perchloric acid.

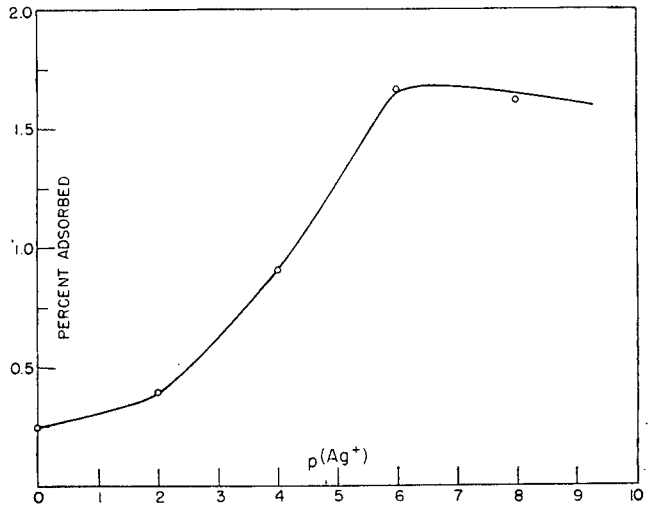

Figure 1. Adsorption on Kirk Pipet

In view of the small amount of silver involved, and because radioactivity offered a sensitive and convenient method of measurement, radioactive Ag^{111} obtained by neutron irradiation of palladium in the Oak Ridge pile was used for this study. Carrier-free Ag^{111} of high specific activity was recovered from the palladium by electroseparation from cyanide solution according to the method of Griess and Rogers (*4*), following which the silver activity was dissolved by electrolysis into a few milliliters of 0.1 *M* perchloric acid for use in the adsorption studies. The concentration of silver in the resulting solution could be calculated as less than 10^{-8} *M* (*4*), but as especially purified reagents were not used, the concentration was probably greater. Standard solutions containing higher concentrations of silver were prepared by adding portions of this tracer solution to known amounts of 2.00 *M* silver perchlorate or dilutions thereof and bringing to volume with 0.1 *M* perchloric acid. Solutions were stored in glass-stoppered bottles coated with ceresine wax in order to minimize changes in concentrations with time.

The following procedure was used to determine the extent of adsorption onto a single 50-μl. Kirk pipet.

The pipet was cleaned with concentrated nitric acid, followed by several rinses with distilled water. It was then filled with 1 M potassium thiocyanate and again rinsed three times with distilled water. The pipet was then filled with a particular solution of silver and the experiment was completed in one of the following ways:

The total activity in a given aliquot was determined by counting one pipetful plus three washes with 1 M potassium thiocyanate by means of an end-window counter, using the technique of Freedman and Hume (*2*) as modified by Goddu and Rogers (*3*).

The losses due to adsorption were determined after expelling and discarding the solution together with three washings of distilled water by combining and counting three washes with 1 M potassium thiocyanate.

Five replicates were taken for each point, at least four of which were usually suitable for counting. The ratios between the counts for the thiocyanate washings and total number of counts obtained from the active solution were taken as the measure of the amount of adsorption which had occurred.

The results are shown in Figure 1. One may judge the reliability of each point from the data for the 10^{-6} M solution of silver. The total activity in 50 μl. was found to be 7727 counts per minute with a coefficient of variation of 2.8%. The activity of the thiocyanate washings was 129 counts per minute with a coefficient of variation of 1.6%. The percentage of adsorbed silver removed by the thiocyanate was therefore 1.67%. Even in the case of the 1 M solution of silver, where the fraction of silver adsorbed was very small, the coefficient of variation for the washings was only 14%.

Whether or not there is a plateau at very low concentrations of silver ion is not certain, inasmuch as the concentration in the "trace" solution obtained by the electroseparation is unknown. If the concentration of silver in the trace solution was as high as 10^{-6} M, the values for the two solutions serve as an excellent check upon each other.

The results obtained in this work indicate that the volumetric error due to adsorption can be important in handling solutions that are only moderately dilute. A similar study with an ordinary 1-ml. pipet having nearly the same surface-to-volume ratio as the micropipet used in the above study gave values which agreed, within the limits with which the ratio could be determined, with those given above.

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Determination of 1,1,1-Trichloro-2,2-bis(*p*-methoxyphenyl)ethane in Milk and Fatty Materials

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THE proposed use of methoxychlor [1,1,1-trichloro-2,2-bis(*p*-methoxyphenyl) ethane] for the control of livestock pests (*1, 6*) made further studies necessary to determine more accurately than has previously been possible the amount of methoxychlor deposited in fat and excreted in the milk of animals treated for livestock pest control. The methods for determining methoxychlor which were previously available were not satisfactory. The Fairing method (*3*), as published, cannot be used satisfactorily for the determination of methoxychlor in fats, but if modified by introducing the Laug-Doble step wherein the dehydrohalogenated residue is taken up in Skellysolve and passed through a column containing a 50–50 mixture of heavy magnesia and Celite to effect chromatographic separation prior to the color development treatment with 85% sulfuric acid, very little interference will be encountered because of unsaponified fat residues.

Prickett and coworkers (*7*) have described a method that is comprised of three steps: saponification and removal of fat, nitration of the dehydrochlorinated derivative of methoxychlor with a 1 to 1 mixture of fuming nitric and sulfuric acids at a temperature below 100° C., and measurement of the red color produced when the nitrated product is treated with sodium methylate. The disadvantage of this method is that a yellow color produced by interfering substances in fatty tissue and butterfat is not constant and therefore interferes with the determination of small amounts of methoxychlor. Both methods make use of saponification for the removal of the fat and as methoxychlor is readily dehydrochlorinated, it is separated as its ethylene derivative.

The method described by Schechter *et al.* (*8*) for separating DDT from fats by extracting a chloroform solution of the fat containing the insecticide with a sulfuric acid–fuming sulfuric acid mixture could not be used because methoxychlor is destroyed by the strong sulfuric acid. Harris (*5*) has suggested that methoxychlor could be separated from fat by dissolving the fat containing the insecticide in *n*-hexane and extracting successively with nitromethane. The authors found this method satisfactory for separating the insecticide completely from the fat. The nitromethane extracts the methoxychlor and leaves the fat in the hexane. An added advantage of this method is that the insecticide is separated as unchanged methoxychlor and is not dehydrochlorinated.

A color reaction suitable for measuring methoxychlor without dehydrochlorination has not been described. The color reaction used by Schechter *et al.* (*8*) for the colorimetric measurement of DDT could not be used, because the nitrating 1 to 1 mixture of fuming nitric-sulfuric acid destroyed the methoxychlor when heated to 100° C. From experience in trying to separate methoxychlor from fat the authors had learned that the methoxychlor was destroyed by the strong sulfuric acid mixture. Therefore, they suspected that the destruction by the nitrating mixture was due to the action of the sulfuric acid. When fuming nitric acid was used alone, the nitration proceeded without apparent decomposition at 100° C. The reaction was complete in 15 minutes, but heating for 1 hour caused no decomposition of the nitrated product. The nitrated product gave the characteristic blue color when treated with sodium methylate. The blue color is not distinguishable from that produced by the tetranitro derivatives of *p,p'*-DDT and TDE [1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane] (*8*). However, the method of nitration used makes the method specific for methoxychlor, as nitration with fuming nitric acid does not produce the tetranitro derivatives of

DDT and TDE. Fuming nitric acid reacts with DDT (*4*) to produce a dinitro derivative, which apparently does not give a color with sodium methylate. When 100 micrograms of DDT (75% *p,p'* and 25% *o,p'*) or TDE are nitrated with fuming nitric acid and the reaction product is treated with sodium methylate, the color is equivalent to that produced by 6 micrograms of methoxychlor. Thus, DDT and TDE when present in small amounts do not cause significant interference.

APPARATUS

Blending apparatus.

Photoelectric colorimeter provided with a filter centering at 590 mμ and matched 14 × 175 mm. test tubes, or any other suitable photometer or spectrophotometer.

SOLVENTS AND REAGENTS

Fuming nitric acid, specific gravity 1.49–1.50.

Sodium hydroxide, 5% solution.

Sodium chloride, C.P., saturated solution in distilled water.

Cotton, extracted with acetone in Soxhlet extractor and air-dried. Stored in dustproof container.

n-Hexane, technical grade, distilled.

Nitromethane, technical grade, distilled.

Benzene, C.P., dry.

Sodium methylate, 10% in dry methanol. Stored in refrigerator. Do not use until optically clear.

Acetone, C.P.

Sodium sulfate, anhydrous.

1,1,1-Trichloro-2,2-bis(*p*-methoxyphenyl)ethane, pure, prepared by recrystallizing commercial methoxychlor twice from ethyl alcohol, melting point 88–89° C.

PREPARATION OF STANDARD CURVE

Dissolve 100 mg. of pure 1,1,1-trichloro-2,2-bis(*p*-methoxyphenyl)ethane in 100 ml. of alcohol (1 ml. contains 1 mg.). Measure 5 ml. of this solution into a 100-ml. volumetric flask and dilute to the mark with alcohol (1 ml. contains 50 micrograms). Into four borosilicate glass test tubes (25 × 200 mm.) place 0.5, 1.0, 1.5, and 2.0 ml. of the standard solution. Evaporate off the solvent on the steam bath and remove any residual traces with a gentle current of air, but do not heat the tubes any longer than necessary. Cool the tubes to room temperature and into each tube put 5 ml. of fuming nitric acid. Place the tubes in a boiling-water bath and heat for 30 minutes.

Remove the test tubes from the water bath and in each tube place 25 ml. of ice-cold distilled water. Pour the acid mixture from each tube into a 125-ml. separatory funnel, rinse the tube with about 25 ml. of water, and pour the rinsings into the funnel. Finally, rinse each tube with two 25-ml. portions of *n*-hexane and pour the rinsings into the separatory funnel. Extract by shaking the separatory funnel vigorously for about 2 minutes. Drain off and discard the aqueous layer, add 10 ml. of water, then drain off the aqueous layer as completely as possible, add 20 ml. of 5% sodium hydroxide solution, and shake vigorously for 1 minute. Drain off the aqueous layer and wash with two successive 10-ml. portions of saturated sodium chloride solution. Drain off closely and filter the *n*-hexane extract through a plug of cotton saturated with *n*-hexane held in a small funnel, into a 125-ml. glass-stoppered Erlenmeyer flask. Wash the funnel with two successive 10-ml. portions of *n*-hexane and filter through the cotton. Place a glass bead in the flask and evaporate the *n*-hexane on a steam bath, removing the last traces with a gentle current of air.

Cool the flask, add 2 ml. of dry benzene, and stopper the flask. Swirl the flask to dissolve the residue, then add from a buret 4 ml. of sodium methylate. Let stand for 15 minutes with occasional swirling, then transfer to the colorimeter tube. Place a rubber stopper in the tube, and then determine the optical density, using a filter centering at 590 mμ and a tube containing 2 ml. of benzene and 4 ml. of sodium methylate for the blank. Construct a standard curve by plotting the optical density, or scale readings which are directly proportional to the optical density, against micrograms of 1,1,1-trichloro-2,2-bis(*p*-methoxyphenyl)ethane. The curve will be a straight line.

PROCEDURE FOR ANALYSIS OF BEEF FAT

Extraction of Fat Sample. Blend 10 grams of beef fat with 125 ml. of *n*-hexane for 2 minutes. (When more than 10 p.p.m. of methoxychlor are expected, take a smaller sample.) Add about 20 grams of anhydrous sodium sulfate and blend for 1 minute longer, then add about 1 gram of Filter-Cel, mix, and transfer to a 400-ml. beaker. Rinse the residual material from the blender into the beaker, using small portions of *n*-hexane. Allow to settle for a few minutes, then filter through a folded filter into a 500-ml. separatory funnel, using several small volumes of hexane to wash the beaker and the insoluble material on the filter.

Separation of Methoxychlor from Fat. Add 50 ml. of nitromethane to the hexane solution of the fat in the separatory funnel, and shake vigorously for 2 minutes. When the layers have separated, drain the lower, or nitromethane, layer into a second 500-ml. separatory funnel containing 50 ml. of *n*-hexane. Repeat the extraction three times, each time using 50 ml. of nitromethane and draining the nitromethane into the second separatory funnel. Shake the separatory funnel containing the combined nitromethane extracts, allow to separate, and drain off the lower layer into a 500-ml. Erlenmeyer flask. Wash the hexane in the second separatory funnel with 50 ml. of nitromethane and drain it also into the flask. Add a glass bead and distill off the nitromethane, which may be collected for re-use, to a volume of about 10 ml. Then evaporate the remainder on a steam bath slowly and carefully to avoid loss of methoxychlor.

Nitration of Sample. Wash the residue from the Erlenmeyer flask into a large (25 × 200 mm.) test tube, using about 15 or 20 ml. of acetone. Add a glass bead and place the tube in a boiling-water bath to evaporate the acetone. Shake or twirl the tube until boiling starts, to avoid bumping. Remove the last traces of acetone with a very gentle current of air. Remove the tube from the water bath, allow to cool to room temperature, add 5 ml. of fuming nitric acid, and proceed as directed in the preparation of the standard curve.

PROCEDURE FOR ANALYSIS OF MILK SAMPLES

Extract a 100-ml. sample of milk by the method described by Carter (*2*). Evaporate the solvent and dissolve the fatty residue in 200 ml. of *n*-hexane. Proceed with the separation of fat and nitration of sample as described for the analysis of fat samples.

Table 1. Recovery of Known Methoxychlor

Sample	Methoxychlor Equivalent of Blank, γ	Methoxychlor Added, γ	% Recovery (Corr. for Blank)
Beef fat		25	98
		50	96
		75	100
		100	97
Butterfat		25	98
		50	90
		75	98
		100	99
Milk	2	25	96
		50	98
		75	91
		100	100

DISCUSSION

Although this method was developed for the analysis of fatty materials, it may also be used for feeds and foodstuffs that do not contain fats.

The method for separating the fat makes it possible to use large samples, which is a great advantage in determining methoxychlor in fatty tissues and milk, where it may be present in extremely low concentrations.

The blank on fatty tissue is very low, but on milk is slightly greater. The color produced by a blank is yellow, not the blue color produced by methoxychlor. However, the yellow color does give a reading on a photoelectric colorimeter. The blank found by the authors for a 10-gram sample of uncontaminated beef fat is equivalent to 1 microgram, and for a 100-gram sample of milk to 2 micrograms of methoxychlor.

A photoelectric colorimeter provided with a filter centering at 590 mμ was used for the color measurements. The standardized test tubes were used instead of the cells because it was possible to read the 6-ml. volume in the tubes. This small volume is advantageous to the sensitivity of the method.

Methoxychlor is slightly volatile and on evaporation of sol-

vents, especially nitromethane, care must be taken to avoid its loss.

RESULTS WITH SAMPLES OF KNOWN METHOXYCHLOR CONTENT

Varying known amounts of methoxychlor were added to 10-gram samples of beef fat and butterfat and to 100-gram samples of milk. The samples were extracted, the insecticide was separated from the fat, and the methoxychlor was determined by the described method. Recoveries obtained are given in Table I.

ACKNOWLEDGMENT

The authors wish to thank T. H. Harris, Production and Marketing Administration, U. S. Department of Agriculture, for helpful suggestions on the separation of methoxychlor from fats.

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Boric Sinter Method for Determination of Sodium Oxide in Alumina

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THE solution of refractory substances such as alumina for the determination of sodium oxide content by the classical J. Lawrence Smith method (*3*, *5*) is a time-consuming procedure that does not lend itself well to the routine chemical laboratory. Jackson (*4*) recently published a procedure embodying heating the alumina samples with hydrochloric acid in sealed tubes at 200° C. This procedure, although an improvement on the classical method, is not particularly rapid, and requires the fabrication of glass tubes able to withstand considerable pressure. Attempts by the authors to develop an acid leaching procedure at atmospheric pressure on finely ground alumina did not prove successful; resultant soda values were invariably low even with very finely ground samples and prolonged digestion periods. However, they have found that a boric acid or boric oxide sinter of alumina provides a rapid method for bringing the soda in this material into solution, the precision of the soda values obtained being as good as by the Lawrence Smith fusion.

PROCEDURE

A finely ground sample of suitable size (0.5 to 1 gram) is mixed well with the appropriate amount of reagent grade boric oxide or boric acid. For a 0.5-gram sample of alumina, 0.85 gram of B_2O_3 is recommended; 1 gram or 1.5 grams of H_3BO_3 per 0.5 gram of alumina also provide a satisfactory mixture. The mixture is placed in a platinum crucible, covered, and heated over a low flame for approximately 5 minutes. The temperature is then increased to full burner flame, and the sinter continued for another five minutes. Too high a temperature at the outset of the sinter can cause mechanical loss of sample.

After the crucible has been removed from the flame and cooled, the sintered mass is knocked into a 250-ml. beaker, 10 to 15 ml. of water are added to the crucible and heated to boiling, and the crucible and cover are policed into the beaker. A few drops of concentrated hydrochloric acid are then added and the mixture is boiled for about 5 minutes to break up the sinter. The solution is filtered on a S. & S. 589 Blue Band paper, and the paper is washed well with hot water.

Soda may be determined on the filtrate using any standard procedure; the authors' laboratory utilizes the Perkin-Elmer flame photometer, with boron added to the standards, but precipitation with zinc uranyl acetate (*1*) is also satisfactory, the determination being finished by direct weighing, or by titration of a reduced sulfuric acid solution of the triple salt with ammonium hexanitrate cerate (or sulfatoceric acid) using ferrous *o*-phenanthroline complex as an indicator.

When zinc uranyl acetate precipitation is used, some boric acid may crystallize out during evaporation of the filtrate to small volume prior to precipitation. However, the boric acid redissolves readily on addition of sufficient zinc uranyl acetate reagent solution. The authors' practice calls for 100 ml. of zinc uranyl acetate solution for a 5-ml. volume of evaporated filtrate; this amount is actually somewhat in excess of that required, but a very satisfactory procedure (*2*) for recovery of uranium values is available. The alcohol washing of the precipitate provides a further safety factor for removal of any precipitated boric acid if less than 100 ml. of zinc uranyl acetate are used. If the determination is finished volumetrically, any precipitated boric acid will be redissolved in the volume used for titration.

Table I. Parallel Determinations of Soda Content of Alumina Samples

Sample No.	Na_2O, %	
	Smith fusion	Boric sinter
1	0.88, 0.83, 0.83	0.82, 0.83
2	0.79	0.80, 0.80
3	0.67, 0.66	0.64, 0.66
4	0.63, 0.62	0.60, 0.63
5	0.54, 0.54	0.52, 0.51
6	0.51, 0.54	0.54, 0.53
7	0.89	0.92
8	0.82	0.82
9	0.77	0.74
10	0.71	0.68
11	0.67	0.66
12	0.62	0.64
13	0.57	0.56
14	0.53	0.53
15	0.51	0.52
16	0.46	0.46
17	0.42	0.41

RESULTS

Table I shows the results of a series of parallel determinations of soda content on seventeen alumina samples by the boric sinter and by J. Lawrence Smith fusion. The soda values shown were obtained by weighing the precipitated $(UO_2)_3.ZnNa(C_2H_3O_2)_9.6H_2O$, a blank being carried through the procedure.

DISCUSSION

While they have had only limited experience in application of the boric sinter procedure to materials other than alumina, the authors feel that it could be successfully applied to a variety of other materials where the Smith fusion attack is ordinarily employed.

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Assay of Samples Doubly Labeled with Radioactive Hydrogen and Carbon

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DURING investigations of various aspects of cholesterol metabolism, a need arose for a simple method of assaying biological specimens doubly labeled with both tritium (H^3) and carbon 14. The apparatus and procedure described below are applicable to problems requiring simultaneous information on both hydrogen and carbon turnover, and have satisfied the authors' needs. Both carbon 14 and tritium specific activities can be determined with a reasonable degree of accuracy with a single sample combustion, and the determinations are readily performed on samples providing approximately 150 mg. of water on combustion.

Siri (*4*) in this laboratory has investigated various methods of assaying tritium activity, and he has found the reaction of lithium aluminum hydride with water suitable and convenient for the generation of hydrogen from water samples containing tritium. The authors are indebted to his experience and to his generous advice during the development of the filling system for tritium assay used in this investigation.

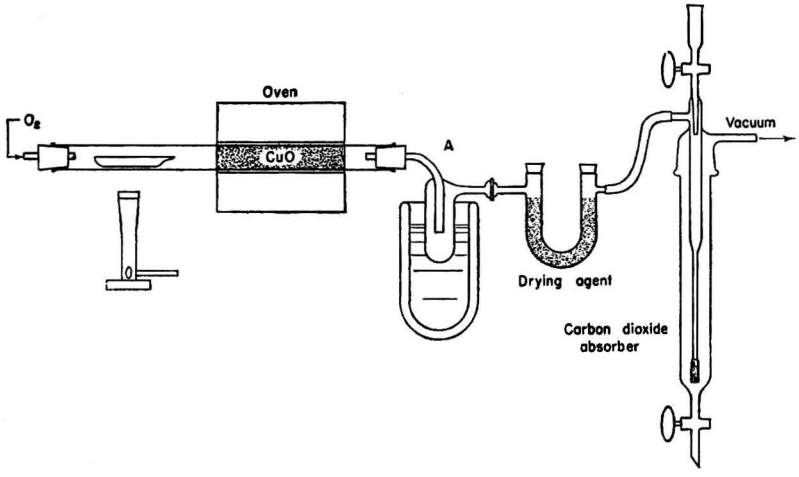

Figure 1. Combustion Train Used for Doubly Labeled Samples

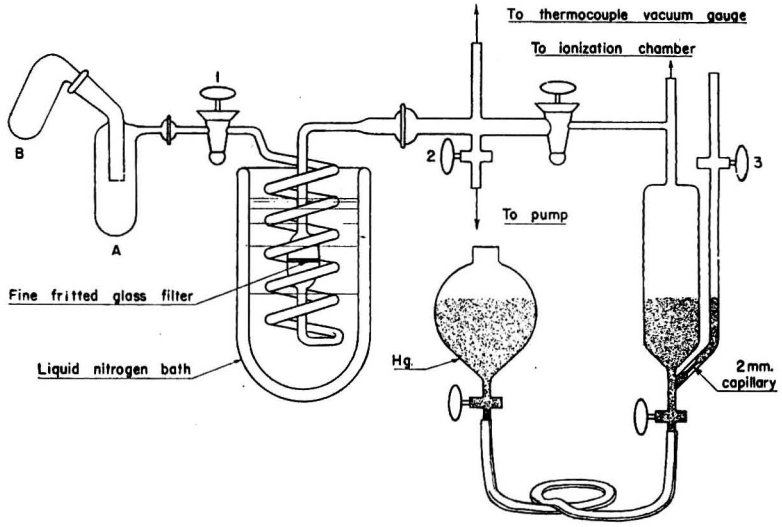

Figure 2. Filling System for Generating Tritium-Hydrogen Samples

PREPARATION OF SAMPLES

The labeled compounds used were cholesterol-C^{14} (random labeled biologically synthesized material), specific activity $6.67 \times 10^{-3}\mu c.$ per mg., naphthoic acid–carboxyl-C^{14}, prepared by carbonation of the appropriate Grignard reagent with isotopic carbon dioxide (*2*), specific activity $8.25\mu c.$ per mg., and tritium-labeled cholesterol prepared by exchange between cholesterol and tritium oxide (*3*), specific activity $0.924\mu c.$ per mg.

An aliquot of an alcoholic solution of the appropriate carbon-labeled compound was carefully transferred to a large quartz combustion vessel, and the solution was evaporated to dryness. After the material was dry, tritium-labeled cholesterol was added in the same way. Finally, a weighed amount of vacuum-dried cholesterol was added to the combustion vessel, this amount calculated to give sufficient water for tritium assay (generally 150 mg.). The samples were varied to give a representation of carbon and tritium activities. Naphthoic acid was substituted for cholesterol after a few experiments in order to conserve biologically prepared material and also to afford samples with a higher carbon 14 activity.

COMBUSTION OF SAMPLES

Figure 1 is a schematic representation of the combustion train used. Trap *A* is submerged in an ice-salt bath to collect the tritium oxide–water sample and is designed to fit directly into the filling system for tritium assay. Quantitative collection of the water formed during combustion is not required.

TRITIUM ASSAY

Figure 2 shows the filling system used for tritium assay.

Trap *A* containing the tritium oxide–water sample for assay was transferred to the evacuated filling system (stopcock 1 closed). Tube *B* contained 3 ml. of a saturated solution of lithium aluminum hydride in anhydrous Carbitol. The water sample was frozen in liquid nitrogen, stopcock 1 was opened,

Table I. Analytical Results

Sample No.	Naphthoic Acid–Carboxyl-C^{14} Activity calcd., $\mu c.$/sample	Activity found, $\mu c.$/sample	% deviation	Cholesterol-H^3 Activity calcd. $\mu c.$/sample	Activity found, $\mu c.$/sample	% deviation
1	0	....	....	0.154	0.148	3.9
2	0	....	....	0.077	0.074	3.9
3	0.64	0.64	0	0.110	0.107	2.7
4	0.65	0.67	3.1	0.110	0.109	0.9
5	1.29	1.20	7.0	0.077	0.076	1.3
6	1.29	1.27	1.6	0.077	0.076	1.3
7	3.23	3.19	1.2	0.038	0.040	5.3
8	3.23	3.18	1.5	0.038	0.036	5.3
9	4.85	4.83	0.4	0.0154	0.0143	7.1
10	4.85	4.74	2.3	0.0154	0.0155	0.6
11	6.47	6.45	0.3	0	....	....
12	6.47	6.49	0.3	0	....	....
			$\sigma = \pm 2.7$			
	Cholesterol-C^{14}					
1	33.35×10^{-3}	31.23×10^{-3}	6.4	0.110	0.108	1.0
2	16.68×10^{-3}	18.04×10^{-3}	8.2	0.077	0.074	3.9
3	50.03×10^{-3}	46.95×10^{-3}	6.2	0.038	0.036	5.3
			$\sigma = \pm 7.0$			$\sigma = \pm 3.9$

and the lithium aluminum hydride solution was outgassed. When outgassing was complete, stopcock 1 was closed and the water sample allowed to melt. The lithium aluminum hydride was quickly added to the water sample (stopcock 2 closed; stopcock 1 open), and the evacuated system was filled with the generated hydrogen-tritium mixture. The sample of hydrogen was then forced into the ionization chamber via a modified Toepler pump to nearly 1 atmosphere pressure. Finally, stopcock 3 was opened and the contents of the ionization chamber were adjusted to atmospheric pressure by balancing the mercury levels in the side arm and pump chamber. The activity in the ionization chamber was determined using a vibrating reed electrometer. The drift obtained was corrected to standard temperature and pressure.

The mercury and glass of the filling system and the brass of the ionization chambers showed no bothersome memory, and pumping for 30 minutes was sufficient to clear the system for the next analysis.

CARBON ASSAY

The carbon dioxide generated during the combustion was collected in sodium hydroxide solution and precipitated as barium carbonate. The barium carbonate, after drying, was plated on aluminum disks by the method described by Calvin *et al.* (*1*). The activity was determined using a Nucleometer windowless-type counter. Several plates were prepared for each sample and the average of several determinations was used in calculating the final activity in each case.

Greater accuracy, if desired, can be obtained in the case of weak samples if the carbon 14 is assayed as carbon dioxide in an ionization chamber instead of using barium carbonate plates.

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(3) Kritchevsky, D., Biggs, M. W., and Freeman, N. K., Univ. Calif. Radiation Laboratory, *Pub.* 644 (1950).
(4) Siri, W., unpublished research.

RECEIVED July 14, 1951. Work sponsored by U. S. Atomic Energy Commission.

Simple Photometric Method for Use with RCA Type EMB Electron Microscope

W. G. KIRCHGESSNER, *Bausch & Lomb Optical Co., Rochester, N. Y.*

IN THE photographic process the success or failure of a print depends upon the satisfactory rendering of the tonal values in the original subject. Consequently, in electron micrography, a correct exposure should be such that the light intensities from the unshadowed area of the subject being photographed fall on the straight-line portion of the $D - \log E$ curve. To achieve this condition satisfactorily a photometer is needed, but because of the low intensity values encountered in this type of work, ordinary photoelectric meters are inadequate. In view of this limitation, a method for obtaining correct exposure data was sought and as a result a simple apparatus was devised, which offers some advantages over previously suggested designs (*1–3*).

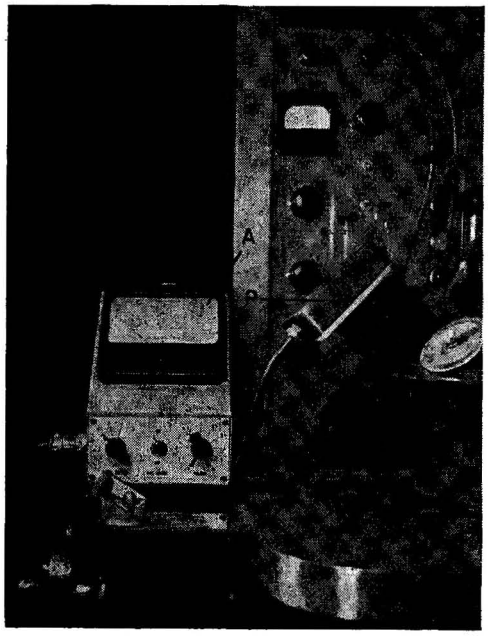

Figure 1. Photometer Unit in Position on Electron Microscope

As illustrated in Figure 1, the photometer consists essentially of three component parts: the lens system *C*, the photoelectric probe, *P*, and the amplifier unit, *A*.

The amplifier unit is a Welch Densichron photoelectric control unit mounted on a bracket attached to the side of the microscope. Light radiations from the fluorescent viewing screen in the microscope are concentrated by two aspheric condensing lenses (equivalent focus = 25 mm.) on the cathode of the photoelectric cell (Cetron CE-25V) which is attached to the lens mount. By this arrangement the photoelectric cell receives only light that is reflected from the screen, and adequate needle deflection on the meter scale is obtained for the low intensity values generally employed.

With the unit attached as described, calibration was made by correlating the relationship between photographic densities, exposure times, and meter readings. Experimentally this was done by exposing a series of test negatives for different units of time at a standard light intensity as determined by selection of some constant Densichron meter value. Control of this variable is maintained by adjustment of the condenser lens current on the microscope. With the test negatives exposed to a series of known exposures and processed under identical and controlled conditions, the responses of the photographic emulsions used were measured optically by means of a polarizing photometer. From these data ideal exposure conditions are quickly defined for various emulsions and thus the amount of light reaching the photoelectric cell becomes a direct measure of the exposure time.

In the application of this method several tests have been made to determine its limitations. From the series of data collected, an average mean deviation of ±6.0% was obtained under the conditions of ordinary use. Because of the deterioration of the fluorescent material on the screen the unit should be calibrated periodically in order to assure satisfactory performance.

The following advantages may be claimed for the device: consistent uniformity of negatives, resulting in the elimination of repeat exposures; and flexibility, in that the unit is easily assembled from readily available parts and may be quickly detached for use in other laboratory problems.

ACKNOWLEDGMENT

Acknowledgment is made to Winifred Steinorth for assistance in accumulating the data in connection with this work.

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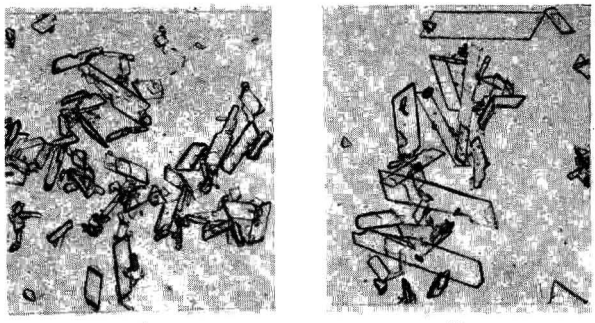
RECEIVED June 7, 1951.

CRYSTALLOGRAPHIC DATA

52. Lanthanum Oxalate Decahydrate, $La_2(C_2O_4)_3.10H_2O$

Contributed by VICTOR GILPIN, Michigan State College, Lansing, Mich., and WALTER C. McCRONE, Armour Research Foundation of Illinois Institute of Technology, Chicago 16, Ill.

LANTHANUM oxalate decahydrate is too insoluble to recrystallize from water. Excellent crystals, however, can be obtained using a procedure adapted from Wylie (*1*). One per cent solutions of oxalic acid and lanthanum nitrate acidified with nitric acid are added dropwise to water maintained at about 50° C. The addition of 100 ml. of each solution to about 100 ml. of water should require about 2 hours. The resulting crystals should be filtered immediately. More dilute solutions yield larger crystals more suitable for single crystal x-ray measurements.



A B

Figure 1. Crystals of Lanthanum Oxalate

A. **Decahydrate as precipitated**
B. **Anhydrous crystals after heating for 3 hours at 220° C.**

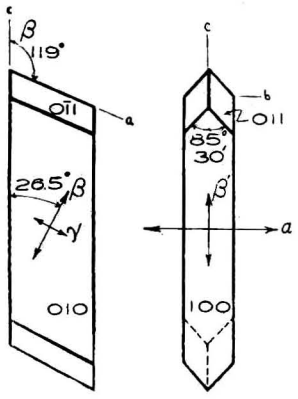


Figure 2. Orthographic Projection of Typical Crystal of Lanthanum Oxalate Decahydrate

Wylie (*1*) describes the oxalates of lanthanum, cerium, and yttrium as "interstitial" hydrates because of their resemblance to the zeolites. Lanthanum oxalate precipitated as described above analyzes to give 10.2 molecules of water. The single crystal x-ray data can be used to calculate a molecular weight and the value calculated corresponds exactly to that of a hydrate containing 10.2 molecules of water. As most of the water of crystallization is lost without apparent damage to the crystal lattice, an attempt was made to determine the x-ray data for the anhydrous form. The results were completely negative; large well-formed crystals of the anhydrous oxalate prepared by heating for 4 hours at 220° C. gave neither a powder pattern nor a single crystal pattern. The anhydrous oxalate is amorphous in spite of its appearance (Figure 1, *B*). In an effort to learn more about the dehydration mechanism during heating of the decahydrate the optical properties, density, and water content were studied as a function of heating time (Figure 3).

Study of these data confirms the results of Wylie (*1*) that the water of hydration is held interstitially; it is not an integral part of the lattice. It also suggests that the water is held in layers parallel to 010. Furthermore, as the water leaves the lattice most of the shrinkage occurs along the *b* axis. The net result is a very large increase in density and a large increase in the alpha refractive index. This collapse of the lattice during dehydration differentiates this type of structure from the zeolite type, since the latter can be dehydrated reversibly. Lanthanum oxalate once dehydrated cannot be rehydrated without complete recrystallization. The anhydrous oxalate is apparently stable in air indefinitely, but when placed in water on a microscope slide quickly transforms through the solution phase to the decahydrate.

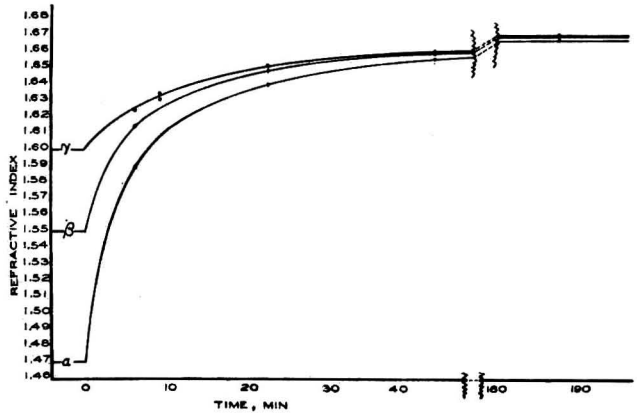


Figure 3. Effect of Heat on Three Refractive Indexes, Birefringence, Extinction, Density, and Water Content of Lanthanum Oxalate

Heating Time, Min.	Temp., C.	$\gamma - \alpha$	α	β	γ
0	20	0.13	1.47	1.55	1.60
6	94	0.035	1.59	1.615	1.625
22	192	0.012	1.64	1.650	1.652
42	213	0.005	1.656	1.660	1.661
60	218	...	...	...	...
187	221	0.003	1.668	1.67	1.671

Extinction, $\beta \wedge C$		Density	Water, Moles
26.5	obtuse beta	2.32	10.2
14.0	obtuse beta	...	...
12.0	obtuse beta	...	...
17.0	acute beta	...	...
...	acute beta	...	6.1
30.0	acute beta	3.30	0.6

In spite of the variable composition of the decahydrate, the optical properties of this phase given below are reproducible and accurate. This is because the phase formed by precipitation as outlined above is always the decahydrate. The water content of this phase is usually about 10.2 to 10.3 moles. The refractive indexes of six different batches of decahydrate precipitated at temperatures ranging from 20° to 80° C. were within the limits of error given below.

CRYSTAL MORPHOLOGY

Crystal System. Monoclinic.

Form and Habit. Rods elongated parallel to *c* showing the clinopinacoid {010}, orthopinacoid {100}, and the clinodome {011}.

Axial Ratio. $a:b:c = 1.233:1:1.084$.

Interfacial Angles (Polar). $011 \wedge 0\bar{1}1 = 87°$.

Beta Angle. 119°.
Twinning Plane. 100.
Cleavage. Parallel to 010.

X-RAY DIFFRACTION DATA
Cell Dimensions. a = 11.91 A.; b = 9.66 A.; c = 10.47 A.
Formula Weights per Cell. 2.
Formula Weight. 722 (decahydrate).
Density. 2.30 (flotation and pycnometer); 2.29 (x-ray).

Principal Lines

d	I/I_1	d	I/I_1
10.55	0.5	2.70	Very weak
6.76	1.0	2.63	0.1
5.28	0.5	2.39	Very weak
5.07	0.5	2.33	Very weak
4.86	0.7	2.29	Very weak
4.57	0.1	2.26	Very weak
4.32	0.1	2.21	Very weak
3.79	0.2	2.11	Very weak
3.58	0.3	2.08	Very weak
3.05	0.5	2.03	Very weak
2.96	Very weak	1.99	Very weak
2.91	Very weak	1.58	Very weak
2.83	0.2	1.54	0.1
2.78	0.1		

(As might be expected with a structure of this type, the powder diffraction lines are broadened and the intensities are difficult to estimate.)

OPTICAL PROPERTIES
Refractive Indexes (5893 A.; 25° C.). α = 1.473 ± 0.002; β = 1.548 ± 0.002; γ = 1.601 ± 0.002.
Optic Axial Angle (5893 A.; 25° C.). $2V$ = (−) 77°.
Optic Axial Plane. ⊥ 010, $\gamma \wedge c$ = 63.5° in obtuse beta.
Extinction. $\beta \wedge c$ = 26.5° in obtuse beta.

ACKNOWLEDGMENT

The authors gratefully acknowledge the assistance of the Research Corp. in making this study possible.

LITERATURE CITED

(1) Wylie, A. W., *J. Chem. Soc.*, **1947**, 1687.

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.

BOOK REVIEWS

A Practical Manual of Rubber Hardness Testing. *A. L. Soden.* 49 pages. MacLaren & Sons, Ltd., Stafford House, Norfolk St., London, W.C. 2, England, 1951. Price, $1.25.

This manual on rubber hardness testing, which compiles available information on various methods for measuring hardness, is most welcome as a convenient reference work. A manual on this subject has long been overdue.

The Shore A2 durometer has not replaced the quadrant Shore instrument in the United States. The A-2 instrument is not as accurate and does not hold its calibration long enough throughout the hardness range to be of practical value.

The Rex gage, it should be pointed out, gives a hardness reading without any change due to creep. A distinct advantage is that the Rex gage can be removed from the rubber and read under convenient light. Some observers who are used to reading hardness on a dial gage have difficulty in reading hardness on a vernier scale.

The SAE-ASTM Technical Committee on Automotive Rubber has shown that conversion for various scales of hardness when applied to synthetic rubber compounds are inaccurate and unreliable. An instrument which would furnish a positive procedure for measuring indentation pressure is highly desirable and would be a distinct contribution to the problem of hardness testing.

H. A. WINKELMANN

Quantitative Organic Microanalysis. *Al Steyermark.* xii + 389 pages. The Blakiston Co., 1012 Walnut St., Philadelphia 5, Pa., 1951. Price, $7.00.

This small volume contains an admirably condensed treatment of the methods of the organic microanalyst. The procedures are mostly those of Pregl modified in detail to adapt them to present working conditions in an active American industrial laboratory. Constant attention is given to minutiae of operations which it must be admitted are important in obtaining reproducibility, especially with average analytical personnel. Details follow implicitly those specified by the Committee for the Standardization of Microchemical Apparatus and the Association of Official Agricultural Chemists, and represent the best standardization now available. Some additional material not ordinarily included in conventional treatises on microcombustion methods is included, notably the Van Slyke manometric methods and some physical property methods. At the end of each chapter is a condensed summary of additional procedures and applications which intrigues the reader's curiosity without quite satisfying it. This section contributes a large proportion of the references, and probably represents most of that which is of interest to the research analytical chemist. This volume should be of great value in training of microanalysts, both in universities and industrial laboratories because of its clear and detailed presentation. It will have less interest as a reference for research workers.

PAUL L. KIRK

Chemische Optik. *Hermann Mohler.* 296 pages. Verlag H. R. Sauerlander & Co., Aarau, Switzerland, 1951. Price, 23 Swiss francs.

This book presents a very basic introduction to the theory and application of optical methods to chemical analysis. The first section synopsizes the physical theories of light, matter, and their interaction in a very elementary manner. Section two mentions those optical measurements utilizing monochromatic light, and the third those depending on spectrally dispersed light. The fourth section concerns itself, again briefly, with the relationship between optical properties and chemical constitution.

In encompassing this wide field of chemical analysis as well as attempting a mathematical presentation of the underlying physical-optical theories, the author is of necessity rather brief. The attempt to familiarize the beginning student with the most recent concepts falls short of this goal by several years. References, in general, are to standard European texts, and not to the journal literature, recent or otherwise. The text is primarily a survey and in this regard presents an elementary review of well-known instruments and well-established methods.

For anyone unacquainted with the ramifications of optical methods in chemical analysis, the book is interesting reading, although lacking in detail. Anyone acquainted with the field will find a survey of fundamentals, undoubtedly already gleaned elsewhere.

HANS J. STOLTEN

Optical Crystallography. *Ernest E. Wahlstrom.* 2nd ed. vii + 247 pages. John Wiley & Sons, 440 Fourth Ave., New York, 16, N. Y., 1951. Price, $4.50.

In the second paragraph of his preface, the author of this sturdy book has chosen to emphasize the contribution of optical crystallography to chemistry. It is appropriate therefore to mention that his point of view throughout is that of a geologist. The

problems and even the opportunities appearing to the chemist are scarcely mentioned. The trait of many compounds to dissolve in immersion liquids—for which no remedy is proposed—is acknowledged only in a quotation from Larsen and Berman. The opportunities of utilizing external form are considered only in a condensed table of directions, where there is an injunction to notice crystal habit. Even when the dispersions of optical directions are treated, effects dramatic and important with many chemical substances, examples are invariably chosen from the minerals.

The high virtue of "Optical Crystallography" lies in its clear presentation of the way that light behaves in anisotropic crystals. An explicit text is formed around a series of illustrations that wonderfully portray the spatial relations between directions, wave fronts, indicatrices, polarized sinusoidal motions, etc., which torment the learner (and perhaps sometimes even the specialist) in this field. Although developments of the past twenty years are almost totally omitted, it can be argued that this is proper, even in the second edition, of a book with the function of providing clear, well-formed instruction in a science which few chemists ever learn. CHARLES PROFFER SAYLOR

Silicate Analysis. *A. W. Groves.* 2nd ed. xxiii + 336 pages. George Allen & Unwin, Ltd., Ruskin House, 40 Museum St., London, W.C. 1, England, 1951. Price, 25s.

This laboratory manual, designed for chemists and geologists, covers the analysis of rocks and natural and artificial silicates, and also contains requisite material on occurrence of the elements, mineralogy, and petrology. The revised edition includes new alternate methods and references to selected methods published since the first edition (1936). The section on geochemical data has been expanded, and that on recalculation of mineral analyses has been completely rewritten.

The importance of proper sampling is stressed and adequately treated. The methods of analysis are mainly established standard procedures supplemented by the author's findings from a long, successful career in this field. The procedures are given in complete detail and reflect the author's appreciation of the attention to details in technique required to obtain accurate analyses.

The chapter covering notes on the analysis of industrially used silicates, phosphate rocks, etc., could profitably be expanded in a future edition. The use of the flame photometer for the determination of the alkalies and alkaline earths is not mentioned. In some cases the methods given are not representative of present-day techniques—for example, copper (page 143) can now be determined by the diethyldithiocarbamate method in the presence of iron and nickel. Nor has the reviewer found it necessary, as stated on page 105, to let periodate-oxidized manganese stand "at least 3 hours" before photometric measurement. These comments are not intended to detract from the over-all value of the book, which should be useful to those engaged in the analysis of silicates and related materials. H. A. BRIGHT

X-Ray Analysis of Crystals. *J. M. Bijvoet, N. H. Kolkmeyer, and C. H. MacGillavry.* xii + 303 pages. Interscience Publishers, Inc., 215 Fourth Ave., New York 3, N. Y., 1951. Price, $8.00.

This is a useful book, in spots a great book, and unfortunately also an uneven book containing many errors due, this reviewer hopes, for the most part to poor translation rather than to careless writing on the part of the distinguished and very capable authors.

The elegance of treatment was a continual delight and should prove an inspiration to the student. Many of the appendixes might better have been integrated into the main text—but this would have required a complete rewriting. Apparently the first part of the book, devoted to fundamental theory, was carried over from an earlier edition without extensive revision, as can be seen from the small number of recent references. The second half, particularly those chapters dealing with results of structure analysis, have been much more carefully worked over and brought up to date.

A cursory first reading turned up about a dozen errors, but to list these would not do justice to this book. It should be in the library of every crystal structure worker. It is a "wise" book.

I. FANKUCHEN

Quantitation of Mixtures of Hemoglobin Derivatives by Photoelectric Spectrophotometry. *Francis T. Hunter.* xx + 226 pages. Charles C Thomas, 301–327 East Lawrence Ave., Springfield, Ill., 1951. Price, $8.50.

This book provides excellent reference material for spectral curves of hemoglobin derivatives and specific methods of calculation, and also gives one unfamiliar with spectrophotometric methods sufficient information to carry out a considerable variety of determinations. However, anyone who wishes to gain a thorough understanding of the principles underlying such determinations will find it necessary to seek other sources.

The contributions of cell thickness and slit width are not developed. The importance of the contribution of scattering and its dependence on the instrumentation is not clarified. The possible value of the near-infrared deserves more attention. As an investigator becomes experienced, he will want to inquire further as to choice of procedures and their attendant limitations. Nevertheless, it is our belief that this beautifully presented material will serve a useful purpose. FREDERICK S. BRACKETT

NEW BOOKS

Directory of Libraries and Information Sources in the Philadelphia area. *Rebecca B. Monego,* ed. 8th ed. 128 pages. Special Libraries Council of Philadelphia and Vicinity, 51 East Garfield St., Philadelphia 44, Pa. $2.25.

Practical Photogrammetry. *H. Oakley Sharp.* 229 pages. Macmillan Co., 60 Fifth Ave., New York 11, N. Y. $3.75.

Ultraviolet Spectra of Aromatic Compounds. *Robert A. Friedel* and *Milton Orchin.* vi + 52 pages of text and 579 graphs. John Wiley & Sons, 440 Fourth Ave., New York 16, N. Y. $10.

Employment, Education, and Earnings of American Men of Science. *United States Department of Labor, Bureau of Labor Statistics,* Bulletin 1027. 48 pages. Superintendent of Documents, U. S. Government Printing Office, Washington 25, D. C. 45 cents.

Vacuum Physics. Symposium Held by Midland Branch, Institute of Physics, in Birmingham June 27 and 28, 1950. Supplement 1, *Journal of Scientific Instruments.* 80 pages. Institute of Physics, 47 Belgrave Square, London, S.W. 1, England. 15s.

ASTM Standards on Bituminous Materials for Highway Construction, Waterproofing, and Roofing. Sponsored by ASTM Committee D-4 on Road and Paving Materials, and ASTM Committee D-8 on Bituminous Waterproofing and Roofing Materials. xi + 329 pages. American Society for Testing Materials, 1916 Race St., Philadelphia 3, Pa., 1951. $3.25.

Southwide Chemical Conference

THE Southwide Chemical Conference was held on October 18, 1951, at Wilson Dam, Ala. Abstracts of papers presented before the Analytical Section are given below.

Chromatographic Studies of Inner Complex Organic Salts. JOHN A. DEAN, University of Tennessee, Knoxville, Tenn.

Inorganic ion exchange chromatography on acid-washed alumina has been extended to the ferrous iron–nitroso R salt complex.• Chromatographic studies of inner complex salts have been initiated. Separation of dithizone complexes have been studied by both adsorption and partition chromatographic procedures.

A New Analytical Method. Radioactivation Analysis. G. W. LEDDICOTTE AND S. A. REYNOLDS, Oak Ridge National Laboratory, Oak Ridge, Tenn.

Radioactivation analysis is a unique method for the detection of impurities in pure chemicals, in metals and alloys, and even in organic substances. It is foremost a method for the determination of trace quantities of elements by the formation of their artificially radioactive isotopes. Remarkable sensitivity may be obtained for many of these elements. Radioactivation analysis is unusually free from interference, since contamination often encountered in conventional methods is negligible. The utility of the analysis, its detection limits, and other pertinent information were appraised.

A Recording Automatic Titrator for Macro and Micro Titrations. M. T. KELLEY, F. J. MILLER, J. L. HORTON, AND J. R. TALLACKSON, Oak Ridge National Laboratory, Oak Ridge, Tenn.

A strip-chart recording titrator has been developed which can be used with syringe burets from 1 to 50 ml. in capacity or with an especially constructed microburet of 50-μl. total capacity. This titrator is especially valuable in titrations involving more than one potential break and in work where it is desirable to have a record of the complete titration curve. The input impedance of the amplifier used is sufficiently high to permit the use of all types of commonly employed electrodes, including glass electrodes. The titrator is constructed in two units connected only by electrical cables, so that it can be readily used for titration of highly radioactive materials without exposing the operator during the course of the titration.

A Microburet for Use in Automatic and Manual Titrations. M. T. KELLEY, H. L. HEMPHILL, P. F. THOMASON, AND F. J. MILLER, Oak Ridge National Laboratory, Oak Ridge, Tenn.

A microburet was described, the principal feature of which is the positive displacement of the titrant by a platinum plunger. The plunger is carefully machined and is actuated by a micrometer-type screw feed. It is calibrated with a scale (from 0 to 50 μl.) of the type commonly found on micrometer-calipers. The plunger works in a chamber constructed of Teflon and the buret is filled by withdrawing the plunger past a hole in the Teflon chamber so that suction can be applied. Since platinum alloy is used for all exposed metal parts, the buret can be used with highly corrosive solutions without any effect on the strength of the titrant.

Determination of Phosphorus by Precipitation as Oxine Molybdiphosphate. J. A. BRABSON AND O. W. EDWARDS, Division of Chemical Engineering, Tennessee Valley Authority, Wilson Dam, Ala.

Scharrer's method for minor amounts of phosphorus, based upon precipitation of oxine molybdiphosphate, was tested for applicability to solutions of high sulfate concentration. Large quantities of sulfate interfered by coprecipitating molybdenum oxyquinolate. The interference was eliminated by dissolving the contaminated oxine salt and reprecipitating.

Merck Graduate Fellowship in Analytical Chemistry

Applications are again being received for the Merck Graduate Fellowship in Analytical Chemistry, financed by Merck & Co., Inc., and administered by the ACS. The annual stipend is $2500. The place of study must be an institution whose undergraduate course of instruction in chemistry is approved by the Society. In Canada, the institution selected must be approved by the Chemical Institute of Canada and the ACS.

A fellowship will be awarded to the applicant believed capable of contributing most to the advancement of the theory and practice of analytical chemistry during the fellowship and in the future. It will be voted contingent upon the successful candidate obtaining acceptance from the institution and professor selected for the study program proposed.

Application blanks may be obtained from the AMERICAN CHEMICAL SOCIETY, 1155 Sixteenth St., N.W., Washington 6, D. C. They should be completed and returned to the Merck Fellowship Committee, at the same address, along with letters of recommendation and transcripts of credits. Deadline date for receipt of all material is March 1, 1952.

The Analyst's Calendar

Symposium on Modern Methods of Analytical Chemistry

The fifth annual Symposium on Modern Methods of Analytical Chemistry will be held at Louisiana State University, Baton Rouge, La., January 28 to 31. The following papers will be given:

Instrumentation. R. H. MÜLLER.
Coulometric Titrations. W. D. COOKE.
Coulometric Titrations with Externally Generated Reagents. DONALD DE FORD.
Activation Analysis. M. T. KELLEY.
Radioactivity Analysis. S. A. REYNOLDS.
Survey of Applications of High Frequency Methods. OLEN NANCE.
Inorganic Microchemistry. P. W. WEST.
Partition Chromatography. L. P. ZILL.
Qualitative Organic Analysis. N. D. CHERONIS.
Quantitative Organic Analysis via Functional Groups. SIDNEY SIGGIA.
Organic Reagents for Inorganic Analysis. FRANK WELCHER.

The talk at the banquet will be given by D. R. Taylor, on "Water—Believe It or Not."

Philadelphia Analytical and Microchemical Group

The Analytical and Microchemical Group of the Philadelphia Section, AMERICAN CHEMICAL SOCIETY, will be held February 7 at 2 P.M. in the Marshall Laboratory, E. I. du Pont de Nemours & Co., 3500 Grays Ferry Ave., Philadelphia. O. Davis Shreve will be chairman of the meeting. J. T. Harris and M. R. Connelly will speak on "Infrared and Ultraviolet Spectroscopic Techniques, Methods, and Applications in the Analysis of Surface Coatings and Related Materials," and O. D. Shreve will speak on "Statistical Evaluation of Reliability of Quantitative Analytical Methods as Applied in Practice in an Industrial Research Laboratory." A tour of inspection of the laboratories will follow the lectures.

Instrumental Methods of Analysis in the Nonferrous Industry

The American Association of Spectrographers is planning a Symposium on Instrumental Methods of Analysis in the Nonferrous Industry, to be held in Chicago in May 1952. Inquiries should be addressed to Robert Raisig, Apex Smelting Co., 2537 West Taylor St., Chicago 12, Ill.

American Society for Testing Materials. Committee D-2 on Petroleum Products and Lubricants, Washington, D. C., February 3 to 8, 1952
Symposium on Analyses Relating to Manufacture of Butadiene. Office of Rubber Reserve and Technical Committee H of ASTM D-2. Washington, D. C., February 1952
Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy. William Penn Hotel, Pittsburgh, Pa., March 5 to 7, 1952
Symposium on Molecular Structure and Spectroscopy. Ohio State University, Columbus, Ohio, June 9 to 13, 1952
Fifth Annual Summer Symposium. Michigan State College, East Lansing, Mich., June 20 and 21, 1952
International Congress on Analytical Chemistry. Oxford, England, September 4 to 9, 1952

AIDS FOR THE ANALYST . . . .

Switching System for Beckman Absorption-Flame Spectrophotometer. A. L. Dunn, F. L. Humoller, and A. R. McIntyre, Department of Physiology and Pharmacology, University of Nebraska College of Medicine, Omaha, Neb.

IN THE studies of biochemical changes in muscle following neurotomy and tenotomy carried out in this laboratory during the past two years [Humoller, F. L., Griswold, B., and McIntyre, A. R., *J. Gen. Physiol.*, **33**, 723 (1950)] extensive use was made of the Beckman Model DU photoelectric quartz spectrophotometer with the flame photometer attachment. Those familiar with the earlier model of the Beckman instrument are aware that the resistor changes necessary to convert it for use with the flame photometer attachment and back again for use in absorption spectrophotometry are time-consuming and require considerable skill and care.

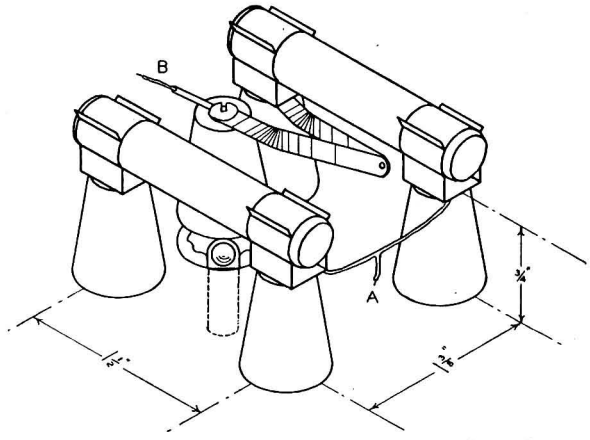


Figure 1. Constructional Details of Switch

In order to eliminate this exchanging of resistors, the authors modified their instrument in such a manner that the 2000-megohm resistor, for absorption spectrophotometry, or the 10,000-megohm resistor, for flame photometry, could be connected into the circuit instantaneously without opening the phototube compartment. In Figure 1 is shown the switch used in the modification.

Only parts obtainable at a radio supply store were used. As available space in the phototube compartment is limited, the pillars on which the switch contacts and the switch blades are mounted can be no higher than about 0.75 inch, although it would be desirable to have the leakage paths longer. The authors employed steatite insulation in their instrument, but polystyrene or material of similar insulating qualities would serve as well. The switch blade and silver contacts were obtainable by dismantling a heavy-duty telephone jack. The clips which hold the resistors on the steatite pillars were taken from mountings for small tubular fuses (Type 3AG or 4AG). The insulating pillar carrying the movable switch blade was mounted on a Centralab K-121 indexing assembly, whose shaft projects through the roof of the phototube case and carries the pointer knob. This indexing assembly assures positive positioning of the switch blade on one or the other contact. The switch is a single-pole double-throw type; one of the stationary contacts is hidden because of the perspective of the drawing. In the authors' instrument the assembly shown in Figure 1 is inverted and mounted on the roof of the phototube compartment. A pointer knob outside the case operates the switch.

Approximate dimensions are given, but they may be varied to suit the available materials. The extreme importance of good insulation must be kept in mind, lest the stability and accuracy of the instrument be impaired. Hermetical sealing of the phototube compartment was maintained by the use of soft-rubber gaskets under the steatite pillars and a soft-rubber grommet around the knob shaft. Electrically the switch assembly carrying the two resistors is substituted for R16 in the circuit diagram of the Model DU spectrophotometer.

A Beckman spectrophotometer–flame photometer modified as described has been in constant use for over two years. The stability of the instrument is unimpaired in any way. Recently National Technical Laboratories have met the need for such a switching device with a resistor switching box which is supplied with current instruments and which may be attached to the older models if desired. The authors' version provides an entirely satisfactory system at a very modest cost for those who may wish to undertake the modification themselves.

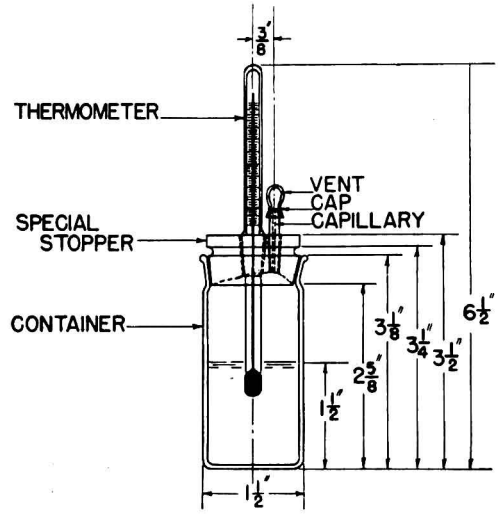
Improved Pycnometer for Powders, Precipitates, and Synthetic Resins. V. F. Downing (present address, Lederle Laboratories Division, American Cyanamid Co., Pearl River, N. Y.), and F. R. Parker, Chemical Department, American Brake Shoe Co., Mahwah, N. J.

MANY special types of glass pycnometers have been devised as aids in obtaining the specific gravity and density of powdered or viscous materials (*1–4*). Although most of these are admirably adapted to the problems for which they have been devised, there seems to be a need, especially among workers engaged in plastics research, for a pycnometer which overcomes the following difficulties:

The narrow necks of most pycnometers make them difficult to load with powdered or viscous materials and difficult to clean after use.

The lack of an attached thermometer as an integral part of pycnometers specifically designed to handle viscous materials makes temperature control somewhat uncertain—a material will eventually come to equilibrium in a constant-temperature water bath, but just when a given material first attains such an equilibrium has frequently been difficult to determine.

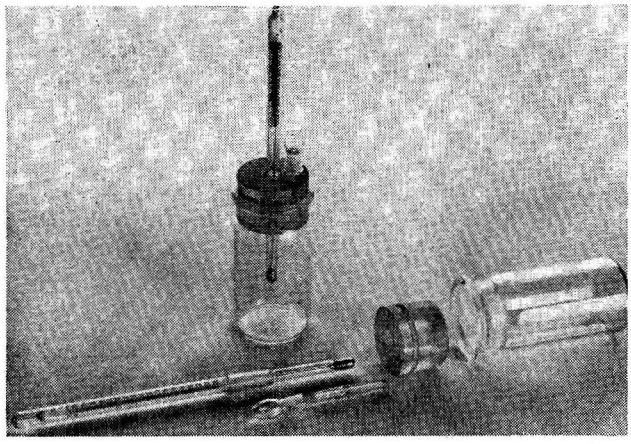
Multiple determinations necessitate the purchase of a number of expensive units or, alternatively, the consumption of a large number of man-hours when using a single pycnometer and its tared duplicate.



The design of the pycnometer presented here seems to be the answer to the above problems, even though the difficulties encountered in the determination of the density of any given

powder, other than the easy loading of the pycnometer with the powder to be tested, have not been solved, and the minor, but universal, problem common to all pycnometers equipped with ground-glass joints—that is, the difficulty in obtaining reproducible seating of such joints— is minimized but not eliminated by the use of alignment marks on the separate pieces of the pycnometer.

Design. The pycnometer illustrated consists of a container similar to a standard weighing bottle, into which is fitted the special stopper which includes a thermometer and a capillary overflow tube equipped with a vented cap. All parts have ground-glass connections which facilitate removal for cleaning. The underside of the special stopper is concave-elliptical, with the apex of concavity at the entrance to the capillary overflow tube, to aid in getting rid of trapped air bubbles.



Test Technique. A large number of containers can be manufactured in such a manner that the special stopper is interchangeable. Therefore, only two special stoppers need be purchased; one for test use and one, tared with its container, to serve as a counterbalance to correct for the adsorption of moisture on the exposed surface of pycnometers during weighing. These containers, which are relatively inexpensive, can be calibrated and marked, and used when multiple determinations are desired. This is particularly important in the case of powders and synthetic resins, where the preliminary preparation is time-consuming but where many samples can be prepared, without much extra effort, in approximately the time necessary for one sample. Usually, in such preliminary preparation, the container remains open and the special stopper is needed only for a short time at the end of the test—during the volume-adjustment and weighing process. If, at any other time, it is necessary to close the containers, standard weighing bottle stoppers can be used.

Accuracy and Reproducibility. The pycnometer is calibrated and used in exactly the same manner as any standard pycnometer (*1–3*). With a laboratory, torsion-type, analytical balance having a sensitivity of ±0.0001 gram and with a constant-temperature water bath controlled to 25.0° ± 0.1° C., this laboratory has checked to ±0.002 gram per cc. the density data forwarded by various resin manufacturers. In many cases, specifications for commercial resins are set up for ranges such as 1.03 to 1.04, 1.20 to 1.30, etc. This appears to be close enough for practical purposes, but occasionally both the supplier and the customer feel the need to check separate batches to three decimal places. The ABSCO pycnometer yields reproducible results to the accuracy noted above, provides for speed in loading, testing, and cleaning, and thereby enables an industrial laboratory to effect an appreciable saving in time and money.

ACKNOWLEDGMENT

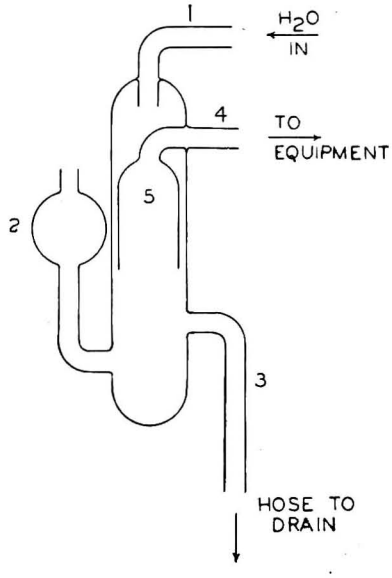
The authors wish to acknowledge the assistance of J. P. Bader, Emil Greiner Co., in the construction of this pycnometer, and of Dorothy Appleton and Theresa Hudock, Metallurgical Department, American Brake Shoe Co., in the preparation of the accompanying illustrations.

LITERATURE CITED

(1) Am. Soc. Testing Materials, Philadelphia, "A.S.T.M. Standards," Designation D 70–27.
(2) *Ibid.*, D 153–39.
(3) *Ibid.*, D 792–48 T.
(4) Fifteen-Year Collective Index, IND. ENG. CHEM., ANAL. ED., 1–15 (1929–43).

A Gas Trap of Large Capacity. Dean R. Rexford, Frick Chemical Laboratory, Princeton University, Princeton, N. J.

A GAS trap of large capacity has been designed for use at atmospheric pressure with water-soluble gases. Its unique advantage is that it creates a slight reduction in pressure within the apparatus to which it is connected. This contributes greatly to safety in handling disagreeable gases, as the gases are allowed to escape only through the trap.



The device has been used in this laboratory for the past two years. It has successfully trapped hydrogen chloride, hydrogen bromide, iodine, and bromine vapors, hydrogen cyanide, and certain lachrymators.

The construction of the all-glass device is simple. It is well to keep the clearance between the bell, 5, and the outer wall to 1 mm. or less; otherwise no dimensions are critical.

Water is allowed to flow in at 1 in sufficient volume to fill the space between the bell, 5, and the outer wall. The bottom part of the main barrel fills up to the overflow, 3. It is important that the device be mounted high enough above the drain to establish a "head" of at least 1 foot above the sink. This is accomplished by mounting the device on a ringstand about a foot above the bench and allowing the overflow water to drain through a length of burner tubing into the sink.

When the device is connected to a closed system, air is drawn in through the side arm, 2. The distance from the bottom of arm 3 to the top of arm 2 regulates the reduction in pressure in the equipment. In the authors' device this was about 0.25 inch. A bulb is blown in arm 2 to prevent water being blown out of the device by sudden increase in pressure within the system.

Water has never been drawn into the system by decrease in pressure in the system (such as sudden absorption of large volumes of gas). The device automatically allows air to enter the system via the side arm, 2.

The device also works well if connected to an equipment via a drying tube.

In substitution bromination reactions a small trap of this design (22 mm. in outside diameter, and 160 mm. in over-all length) trapped hydrogen bromide at the rate of 1 mole per hour. To all appearances, the absolute capacity of a trap of these small dimensions lies well beyond this limit.

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The 0.01° C. Sargent Constant Temperature Water Bath, which is employed in many laboratories throughout the world where a precise, reliable thermostat is required, is now being supplied with an improved relay unit and heating system. The central heating and circulating unit of the bath is now equipped with three cylindrical heating elements rated at 200, 300 and 400 watts respectively. The 200 watt heater is controlled by the No. 81835 mercurial thermoregulator through a thyratron tube and saturable core reactor in the relay unit. (The use of a saturable core reactor obviates the difficulties commonly encountered with mechanical relaying systems such as pitted contacts, broken moving parts and freezing.) By means of a control mounted on the panel of the relay the output of this heater can be varied from the full 200 watts to approximately 60 watts, thus permitting such adjustment of the heater output that positive overshooting of the regulatory temperature is minimized. With the improved relay system this bath can be adjusted to a precision of ±.005° C. when operating in the vicinity of 25° C.

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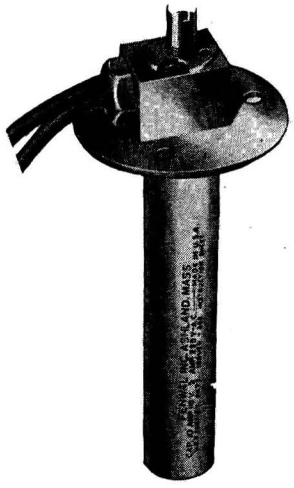

The THERMOSWITCH Control is constructed with two silver contacts mounted on, but electrically insulated from, curved nickel-iron struts of low expansion coefficient. This assembly, known as the element assembly, is then mounted under tension or compression in a seamless drawn brass or stainless steel tube. The amount of tension or compression is variable, depending on the position of adjusting sleeve and the temperature of the shell. The control is calibrated at a given shell temperature by turning the adjusting screw until the contacts separate. Changes in temperature cause the shell to expand or contract which exerts more or less tension or compression on the struts causing the contacts to make or break.

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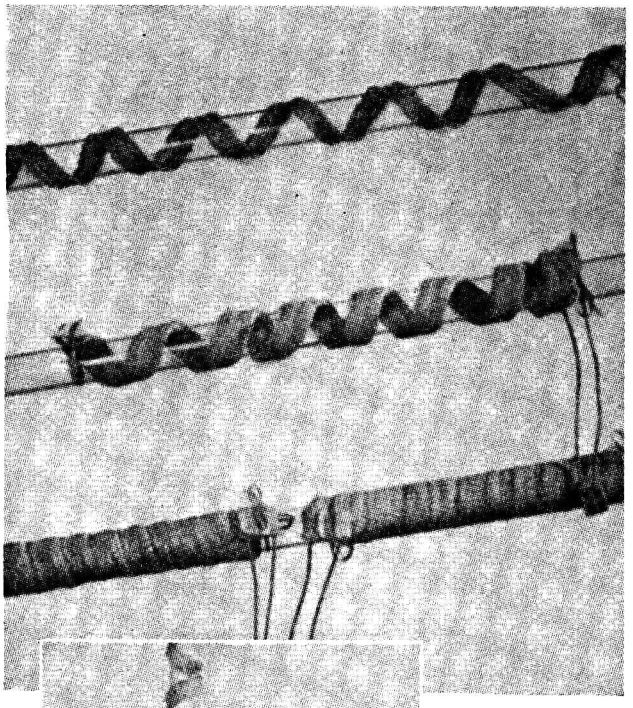


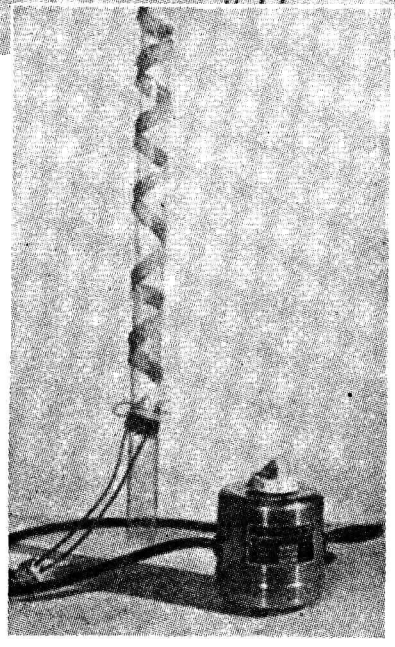
for laboratory applications and for use in pilot and production plant

These tapes consist of one or more fabric bands of resistance wire separated and bordered by bands of high temperature resisting glass fibre yarn. The width and length of the various tapes are carefully determined by the curren carrying capacity of the resistance wire. The surface loading of standard heating tapes has been arranged approximately at 2½ watts/inch² (0.4 watts/cm²) area of tape. This wattage concentration enables temperatures of 400 °C. and over to be reached inside a glass tube of 2 mm. wall thickness.

The application of the tape by simply winding it around the body to be heated makes this new product a most convenient piece of equipment. The tape can be wound with edges adjoining or with any suitable pitch.

All tapes are fitted with lead-in-wires terminating in a connector for easy connection to the mains. A suitable control devise such as a variable auto-transformer or rheostat should be employed. The tape can be held in position by means of glass laces provided at both ends.

Special tapes can be made to specification up to 18 watts/inch². A number of individual tapes should be employed in preference to one of excessive length.

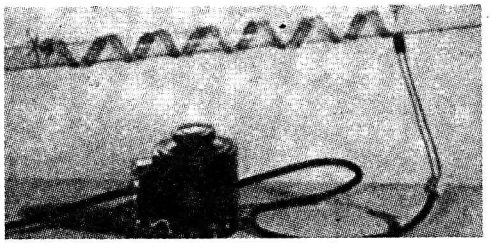


Three principal designs are available

1 Uninsulated

In this construction the current carrying resistance wires are in direct contact with the surface to be heated. (It is important for care to be taken to prevent overlapping and accidental contact.)

As it is possible to look through this tape, it will be of the greatest value for research work when wound on a transparent surface, but heat losses will be more pronounced than with construction (2).



2 Insulated on One Side

This tape is just as simply applied, with direct contact between the resistance wire and the surface to be heated as in construction (1), but heat losses to atmosphere are greatly reduced by the addition of a layer of knitted glass yarn on one side. The tape can be wound on to itself but care must be taken as in construction (1) to wind it directly on to insulating surfaces only.

3 Insulated on Both Sides

This type is constructed of two insulation layers of knitted glass yarn with the current carrying bands in the centre. The type can be safely wound on to metal thus making it especially suitable for heating steel tubes, valves, nozzles and other conducting surfaces. Heat losses to atmosphere are minimized.

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HT.103	"	150	76	450	2-3	16.65
HT.104	"	180	89	500	2-6	19.25
HT.201	Insulated one side	90	25	100	0-8	11.40
HT.202	"	125	64	250	1-5	14.90
HT.203	"	150	76	450	2-3	20.15
HT.204	"	180	89	500	2-6	22.95
HT.301	Insulated both sides	90	25	100	0-8	14.70
HT.302	"	125	64	250	1-5	18.75
HT.303	"	150	76	450	2-3	26.45
HT.304	"	180	89	500	2-6	29.40

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INSTRUMENTATION

A chemical oscillometer, a cold cathode pilot relay, and a complete new line of miniature precision potentiometers have been made available to the analyst

by R. H. Müller

THE use of radio-frequency oscillators in electroanalytical research is increasing and, until recently, no commercially available equipment was to be found for such studies. Of the many circuits that have been proposed, most of them yield results that are characteristic of the circuitry, the frequency, and the mode of balance or deflection which is employed. The information so derived is empirical, a complex function of conductance, dielectric constant, absorption effects, etc. At ultra-high frequencies, capacitative effects predominate. Despite these complexities, the behavior of liquids and solutions in a radio-frequency field is susceptible to very sensitive measurements and without the encumbrance and complication of electrodes.

Although much has been said about the ease with which conductance titrations can be made with such equipment, we still suspect that conductance titrations have little attraction in modern instrumental methods of analysis. They have always possessed a degree of charm to the academic mind, they are illustrative of sound physicochemical principles, but because they invariably require plotting of the measurements for accurate results, they are employed by the analyst only when all other methods fail. We cannot escape the conclusion that these improved methods will best serve the analyst when they are used in less conventional applications such as the control of processes, for checking the effluents of ion exchange or chromatographic columns, or for the empirical analysis of binary or ternary mixtures of nonelectrolytes.

Chemical Oscillometer

In several respects, the resources of electronic circuitry are far beyond our means of applying them intelligently to the needs and potentialities of analysis. It is doubly encouraging when an instrument manufacturer undertakes to develop equipment for the convenient measurement of these phenomena, particularly when its most profitable means of employment is still undetermined. The Sargent Model V chemical oscillometer is a well-engineered example of this class. We like to look upon it as a challenge to the progressive analyst. Let him take this instrument and besiege the barriers of analytical chemistry's unsolved problems.

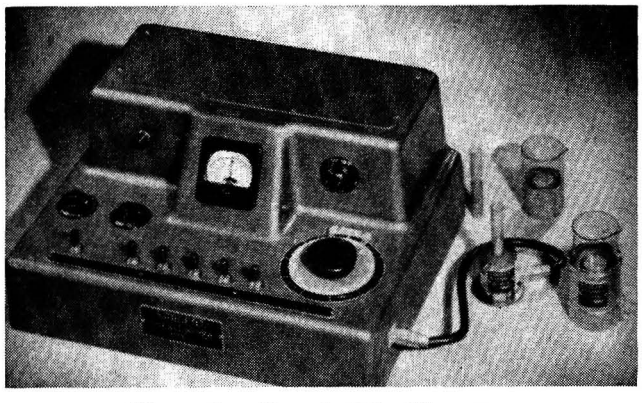

Figure 1. Chemical Oscillometer

As shown in Figure 1, the Sargent chemical oscillometer is a self-contained 5-megacycle oscillator with Amphenol connectors to a variety of measuring cells. In terms of dielectric constants between that of air and water, which we infer to be some 80 units, the oscillometer possesses a scale range of some 24,000 units, reproducible in so far as instrumental characteristics are concerned, to 1 unit. The variety of cells is illustrated in Figure 1 and in none of these is there any direct connection with the liquid or solution under measurement. The total working scale is 32,000 scale units, applied by a multiple-turn dial and additive range switches. The instrument has internal range checking standards. Small and large cells are supplied, one for samples of 5 to 12 ml. and the other for titrations.

For applications to those titrations normally considered as conductometric or potentiometric, the sensitivity of an end-point indication is better in the lower range of conductivities, in general, of those concentrations which are of the order of 0.01 *N*. The titration cell will accommodate a glass stirrer under continuous operation without interfering with the accuracy of the measurement.

Cold Cathode Pilot Relay

Burlingame Associates, 103 Lafayette St., New York 13, N. Y., announce a number of developments of the companies which they represent, all of which command the attention of those interested in instrument components. One of these is a cold cathode pilot relay. For a long time, it has been customary to use vacuum tube relay devices for sensing minute unbalances in a system, and using the output to

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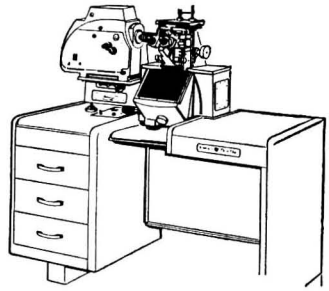

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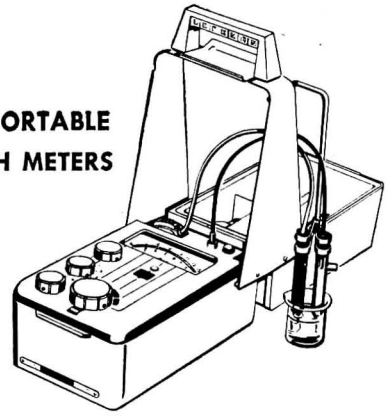

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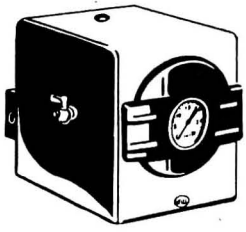

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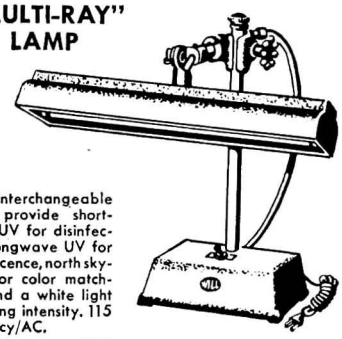

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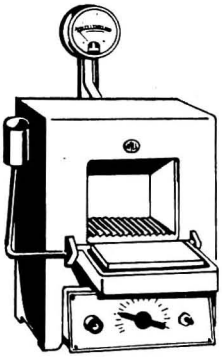

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(Temco Model RCE) One of six sizes available. Operates at any temperature from 350° to 1850°F. Solid aluminum, with removable heating chamber 4¾″ wide, 4¼″ high, 6″ deep. For 115 V/AC.

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INSTRUMENTATION

control heavy duty equipment. The classical example has been thermostatic controls, in which the vacuum tube assembly provided an essentially "no current" regulation of sensibly heavy heating currents. Industrial practice has required long-term and trouble-free service, and in this sense, vacuum tube regulators, although vastly superior to the older mechanical arrangements, have shown residual deflects primarily due to a variable and unpredictable cathode and heater life. Another defect was the limited degree to which these relays could be adapted to a wide range of signal input resistance.

The new development is the cold cathode pilot relay made by the Haledy Electronics Co. This relay uses the Type TT-1 cold cathode triode which has no heater and has a cathode of practically unlimited life. No transformer is required and the circuitry is correspondingly simplified. The relay will operate over any input resistance from a dead short to 10 megohms and with leads from the control device of almost any desired length. The input control current has a maximum value of 2 microamperes. The output of the cold cathode triode directly operates a S.P.D.T. relay having a contact capacity of 5 A., at 115 volts a.c. Under these conditions, the maximum gain of the system could be rated at 2,500,000. For circumstances under which heavier power must be controlled, a Haledy mercury contactor is available which has a rating of 30 amperes, at 115 volts a.c., or 20 amperes at 220 volts a.c.

An additional advantage of the cold cathode relay is its instantaneous action, because no preliminary warm-up or stabilization period is required. The normal output of the cold cathode triode in this control device is 15 ma. through a load of 2500 ohms.

The specifications for the standard model SS cold cathode electronic pilot relay are summarized as follows: input resistivity range, 0 ohm to 10 megohms; maximum input current, 2 microamperes; maximum input lead length, unlimited; power requirements, 2 watts, 115 volts, 60 cycles, one side grounded; relay, S.P.S.T. contacts rated at 5 amperes at 115 volts 60-cycle; electronic tube; one TT-1 cold cathode triode; case, 18-gage drawn steel, wrinkle gray

(*Continued on page 28 A*)

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The ultra-modern design of the Coleman Compax offers the chemist these unusual features.

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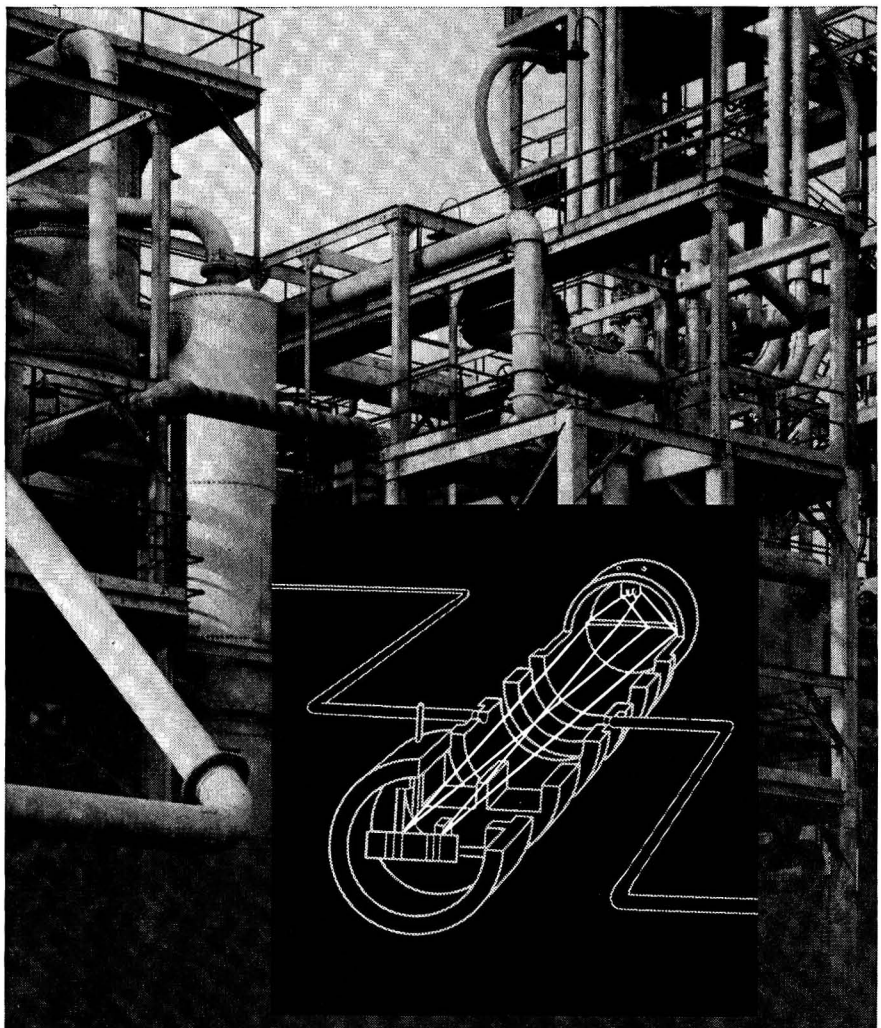


IN STYGIAN DARKNESS
THE SHADOW OF A VAPOR
THINKS FOR A GIANT

Infrared shadows, cast by process gases in the sealed cells of a lightless chamber, permit critical concentrations of a gaseous component to be recorded and to control industrial processes through the Baird Associates Plant Stream Analyzer.

This sensitive, accurate, reliable instrument has proved its worth in control applications involving: n-Butane in methane, ethane, propane, iso-butane, CO, and CO_2; methane in natural and manufactured gas blends; carbon dioxide in expired air; acetylene in 14-component mixture; methane in 14-component mixture; carbon dioxide in 7-component mixture; hydrogen cyanide in 8-component mixture; ammonia in 7-component mixture; acetone in air; acetylene in hydrogen cyanide.

Your process control may benefit by use of the Baird Associates Plant Stream Analyzer. Bulletin 36 gives detailed information; ask us about the use of this instrument in your control problems.

Baird Associates, Inc.
INDUSTRIAL PHYSICISTS
33 UNIVERSITY ROAD CAMBRIDGE 38, MASS.

INSTRUMENTATION

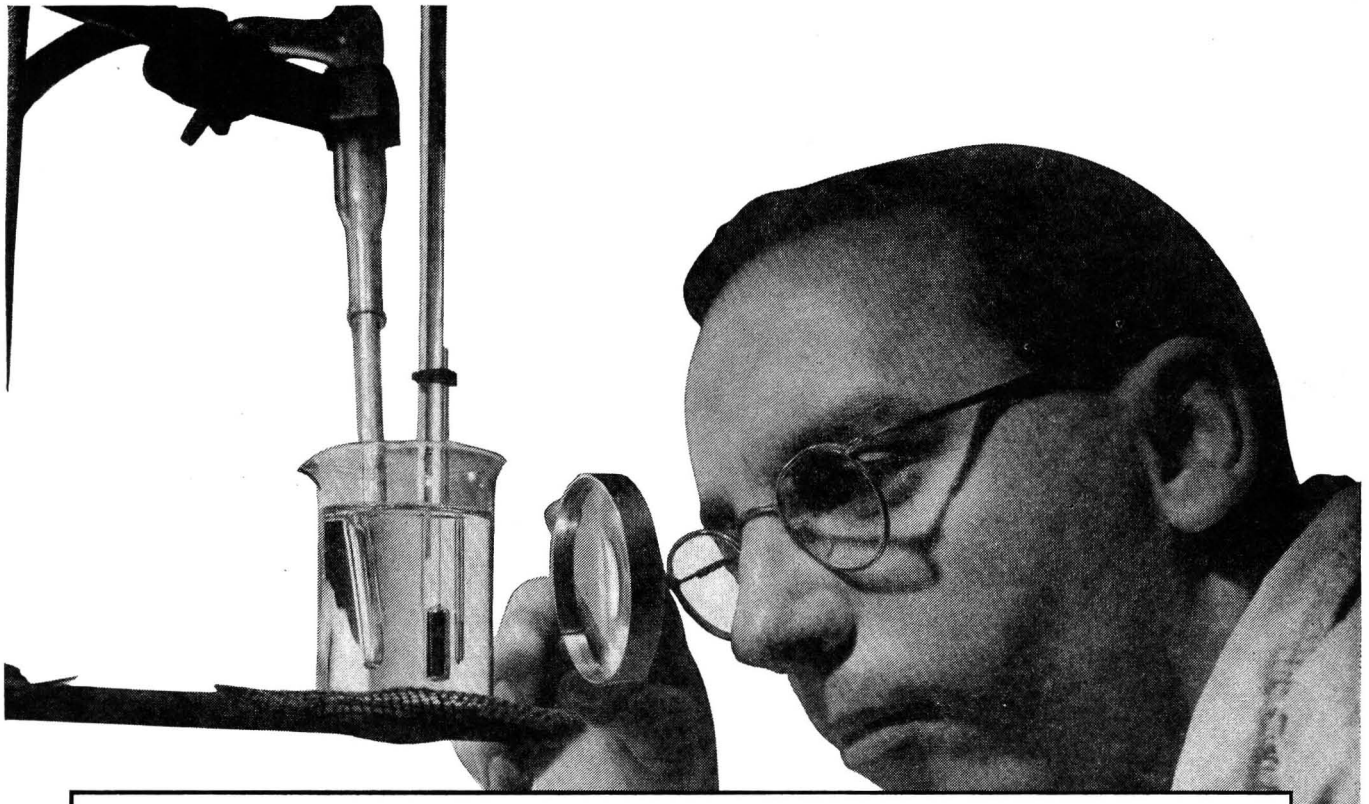
finish, knockouts provided, tamperproof, locking means provided.

At a price of approximately $35, this reliable control unit offers many control possibilities in instrumentation at an attractively low cost figure.

Miniature Precision Potentiometers

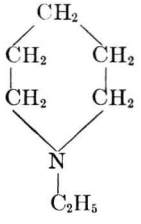
Burlingame Associates also announce a complete new line of miniature precision potentiometers manufactured by the Standard Electronics Mfg. Co., Los Angeles. While the basic applications of these devices include guided missiles, telemetering, computers, and radar firing control, they are suited for any applications requiring a miniature precision potentiometer. The Type F potentiometer is available in the minimal dimensions of 1 × 1 × 0.4 inch of rectangular form and is unique in both mechanical design and operation. The winding form lies lengthwise in the case and is a rhombus in cross section with the contact wiper moving along one of the obtuse angled edges. The wiper is moved by a lead screw which can have as little as three turns (1080°) for full travel or as many as 32 turns (11,520°) for full travel. Any units which have the same type lead screw can be ganged and the windings may be tapped. These units are available in resistance values from 100 to 250,000 ohms with power ratings from 0.25 to 2 watts. Depending upon the range, the maximal length of the device can be 3.5 inches and a maximal width of 0.625 inch. The Type SR is indeed miniature. It is $^5/_8$ inch in diameter and $^{27}/_{32}$ inch long over the terminals. It is rated at 0.5 watt and can be furnished in resistance values from 100 to 50,000 ohms.

In general, these units are designed to operate over a temperature range of −67° to +165° F., but in some designs alkyd plastic cases can be supplied which extend the upper range to +300° F. Resistance tolerance is normally 5%, but can be supplied to 0.5%. Linearity tolerances are normally 1%, but 0.1% can be furnished. No information is available on the torque requirements and it is to be inferred, perhaps, that these devices are not competitive with the micro-torque type such as the Giannini version. Their unique construction and small size should furnish another useful tool.



3 OF THE MORE THAN 3500 EASTMAN ORGANIC CHEMICALS

No piperidine drought...



N-Ethylpiperidine (Eastman 5866) forms a 99+% pure salt of penicillin G from penicillin G of purity as low as 80%. Several years ago a method using this fact was officially accepted for the certification of crystalline penicillin G. We shall be glad to send you an abstract of it. It was fortunate for penicillin-determiners that at the time we made up a goodly quantity of N-ethylpiperidine, for shortly thereafter (the reasons being buried in complicated chemical industry economics) the piperidine from which it is made simply disappeared from the bulk chemical market. The danger of exhausting our stock of N-ethylpiperidine is now past, however, for we have just had a batch of piperidine synthesized to our order by a bulk chemical producer. It's ready also for those who need piperidine itself.

No vague end-point...

Methyl Orange-Xylene Cyanole Solution (Eastman 2216) is a new entry you'll find in a new revision of the Eastman Indicator Chart, a work you probably first encountered along about your sophomore year. The xylene cyanole is a blue dye that converts the familiarly vague yellow-through-orange-to-pink color change of methyl orange to a much more sensitive change from green to magenta in the course of three drops at pH about 3.8. (The new chart is 11″ x 14″, gives preparation directions, and should be easier on the eyes in looking up what indicator goes through what color change over what pH range. We'll be happy to send you a copy with our compliments.)

No peanuts...

$CH_3(CH_2)_{18}COOH$

Arachidic Acid (Eastman 2538) gets its name from *Arachia hypogaea,* the peanut, which fact naturally would suggest peanut oil as a source. This turns out to be a poor hunch if you're after a pure compound because you have the problem of separating out this one particular C_{20} fatty acid. We find it's easier to start with octadecyl alcohol, halogenate, treat with ethyl malonate, hydrolyze, decarboxylate, and there we are. It would be interesting to know how the peanut does it. The product's prime value is in studies of variation in fat properties with chain length. It could also make a very hard and very expensive soap.

Besides these three, there are over 3500 other organics you can get from *Distillation Products Industries,* Eastman Organic Chemicals Department, 611 Ridge Road West, Rochester 3, N. Y. (Division of Eastman Kodak Company).

DPi

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Gives Continuous Service for Years

Without Dismantling or Replacement of Parts.

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Not necessary to take pump apart to quickly and conveniently clean and change oil.

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33.4 liters of free air per minute

LARGE OIL VOLUME
Protects mechanism from Corrosion and Clogging.

EFFICIENT CONTINUED OPERATION over long periods.

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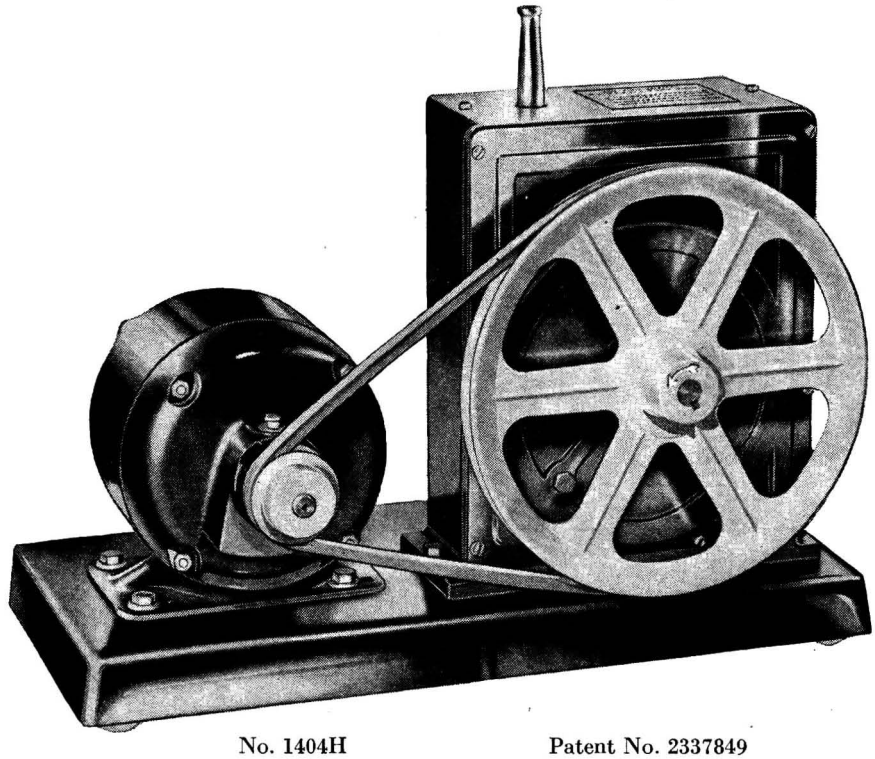

No. 1404H Patent No. 2337849

This pump is expressly designed for vacuum distillation in the organic laboratory. Its large capacity of 33.4 liters of free air per minute materially increases the speed of distillations and the simplicity of its construction insures long life and continuous operation. One of the features of this pump that will appeal to the chemist is the provision for cleaning and changing the oil without taking the pump apart. All that is necessary is to remove the thumb screws which hold the top plate and if the oil has not become too thick with the impurities from distillation processes, the oil in the reservoir may be drained out or it may be poured out by tipping the pump. The flushing oil of low specific gravity and low vapor pressure may then be introduced by placing a rubber tube from the inlet on the top of the pump to the oil container and by turning the pump by hand the oil will be drawn through the pump and this may be removed in the same manner as the old oil. The new oil may then be run into the pump and the pump is again ready to operate. The whole operation requires only a few minutes.

The large volume of oil which is provided in this pump dilutes the vapors which are a product of the distillation and protects the mechanism of the pump from corrosion and clogging. This pump has been found to be particularly efficient in distillations requiring exceptionally long continuous operation. The movement itself is the same movement that has been used in almost every large university in the country and has proven highly efficient. Over forty of these pumps are in operation at the University of Illinois alone. The addition of the large oil reservoir and the greater volume of free air capacity has increased the value and utility of the pump for vacuum distillation purposes. One of these pumps has been utilized in production requiring daily operation for a period of five years, continuing to provide a rapid vacuum of less than .02 mm. on the large capacity vacuum system and has never required dismantling, or the replacement of any parts.

1404. **PUMP ONLY.** Not mounted on base. Complete with grooved pulley for special "V" belt, supply of oil and directions for use but without belt. **Each, $70.00**

1404F. **PUMP, Motor-Driven.** Mounted on cast iron base with 1/3 H.P. motor, V belt, belt tightening device, connecting cord and switch. For 110 volts D.C. **Each, $135.00**

1404H. **PUMP, Motor-Driven.** Same as No. 1404F but for 110 volts A.C. 60 cycles. **Each, $103.00**

1404I. **PUMP, Motor-Driven.** Same as No. 1404F but for 220 volts A.C. 60 cycles. **Each, $103.00**

Correct tubing for connections **No. 5518B,** 7/16 inch bore, 5/16 inch wall.

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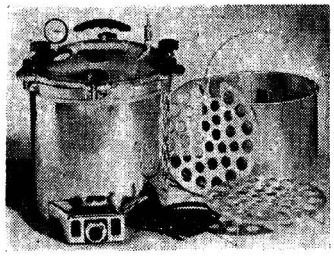
Laboratory Autoclave

A new electrically heated 6-gallon autoclave has been introduced by Andrew Technical Service. Designed for laboratory operations which require elevated temperatures in a water-vapor atmosphere, the autoclave may be used for experimental work or as a portable sterilizer.



The apparatus has a cast aluminum body and cover. The pressure-temperature gage reads from 0 to 30 pounds per square inch, showing corresponding temperatures. The safety release valve automatically opens if the pressure exceeds 21 pounds per square inch (approximately 261° F.). The metal-to-metal closure eliminates the need for troublesome gaskets. An aluminum wiring canopy protects the control components, and a red pilot light indicates when the equipment is in operation.

The apparatus measures 18 inches high and 16 inches in diameter. It comes ready to operate with an aluminum container, 11.5 inches in diameter and 8.5 inches deep, and a trivet for supporting instruments, tubes, flasks, and other equipment. **1**

Gages for Sheet Materials

Two new absorption and back-scatter beta gages for the low-cost determination of the weight per unit area of sheet materials have been developed by Tracerlab, Inc. The absorption beta gage determines weight changes in sheet materials (paper, plastics, rubber, thin metal sheets) by means of a small beam of beta rays. These rays are emitted from a sealed radioactive source and pass through the sheet to be measured. The gage, in effect, weighs a small area of the moving sheet by means of a beam of radiation. If the density of the material is maintained constant, the meter can be calibrated in units of thickness, thus making the gage a sensitive thickness-control instrument. Beta gages are unaffected by the speed of the moving material and do not contact the material being measured. They are capable of use with extremely thin materials which cannot be measured by other methods.

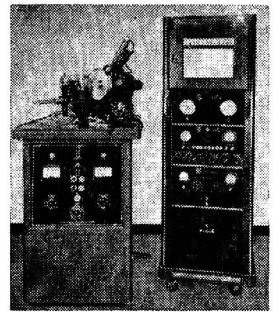
Tracerlab's back-scatter beta gages offer advantages for many installations because they are mounted on one side of the sheet only. Back-scatter gages use the same console and recording apparatus as absorption types, but operate on a slightly different principle. **2**

Triallyl Cyanurate

The American Cyanamid Co. is offering a new monomer, triallyl cyanurate, in pilot plant quantities. The most promising applications of the compound are in the field of plastics and resins. For example, mats prepared by the polymerization of triallyl cyanurate on glass cloth have high flexural strength even at temperatures above 230° C. Since the compound is compatible with many other monomers and with alkyd resins, copolymerizations can readily be carried out. Such polymers and copolymers are recommended in applications requiring superior heat and chemical resistance. **3**

X-Ray Diffraction Spectrometer

An improved recording x-ray spectrometer with wide-range goniometer is now available from the Research and Control Instruments Division of North American Philips Co. The complete assembly consists of three components: a basic x-ray diffraction unit, a Geiger-counter goniometer, and an electronic circuit panel with strip-chart recorder. The new instrument, used for x-ray powder diffraction work and fluorescence analysis, incorporates an x-ray optical arrangement which gives high resolution.



The basic x-ray diffraction unit is designed to operate on 200 to 240 volts, a.c., 50 or 60 cycles, with full-wave rectification and facilities for visual indication of tube operation. The x-ray tube and transformer are water cooled, and the

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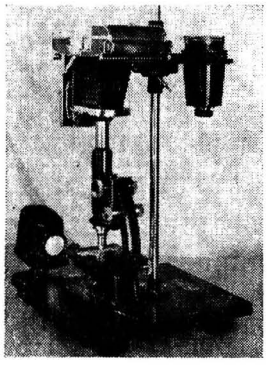
system has a high-flow-rate filter, pressure regulator and gage, and automatic solenoid cutoff protection for high and low pressure limits and flow rate. Safety interlocks are provided on all doors and removable panels. The generator has a key-operated main switch, separate high-voltage control switch, and automatic sequence relay operating system. The unit has an exposure timer, an operating time totalizer, and power outlets for accessory equipment.

The goniometer is designed to scan and analyze x-ray diffraction spectra of specimen materials by divergent-convergent beam-focusing geometry. It provides for accurate measurement of angles from 180° to −38°, with a useful x-ray diffraction range from 38° to 165°. The goniometer scanning has a horizontal axis and a synchronous motor driven in either direction at five different speeds. Stop limits and operational controls allow single-scan or oscillatory scanning in any part of the range.

The Geiger counter has a thin mica window, a high volume sensitivity, high counting rate, and a life expectancy in excess of 100 billion counts. The electronic circuit panel includes a Brown strip-chart recorder, timer, and clock panel, scaling and rate meter circuits, impulse counting and interpolation system, d.c. Geiger counter power supply, and specially designed voltage stabilizer. **4**

Camera Support

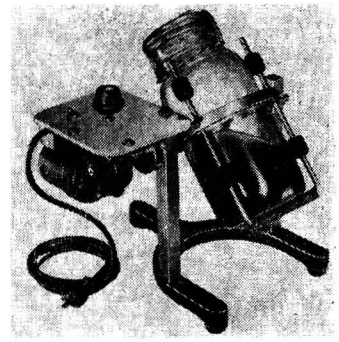
Central Scientific Co. offers a support for the Polaroid Land camera, which makes possible the production of photomicrographs within a matter of a minute or so. Objects seen under the microscope may be photographed for the permanent record, and the finished picture examined almost immediately afterward. Any make of microscope may be used, since the height of the camera is adjustable and can be positioned as required.



First the camera is positioned over the body tube of the microscope, with the film and paper carriage open and the ground-glass plate in position instead of the film. After the camera has been centered and its distance set for infinity, the microscope is adjusted to focus an image of the object sharply onto the ground-glass screen. Without the setting of the microscope being changed, the viewer is brought into position over the eyepiece. After the lens of the viewer is centered with the aperture of the eyepiece, the glass screen is adjusted upward or downward until the image of the object comes into sharp focus. This adjustment is fixed with the lock ring of the viewer. The viewer is now the optical equivalent of the camera and will remain such as long as the same camera is used and the position of the viewer is unchanged. Film and paper are loaded into the camera, and the unit is ready for taking photomicrographs. **5**

Motor-Driven Tumbler

Andrew Technical Service announces a new portable motor-driven tumbler that can accommodate a 1-quart glass jar. The jar is mounted in a cage which is rotated by a gear-head universal motor with rheostat control from 20 to 110 revolutions per minute. The end-over-end action of the jar subjects the contents to a vigorous displacement for efficient agitation and mixing. When the rotation is stopped, the jar can be brought to an upright position by a few turns of a control knob. All support components of the tumbler, other than the horseshoe base, are cadmium plated for corrosion resistance.



The jars are of the Ball type, with glass cover clamped tight against a gasket of rubber, Tygon, or neoprene. The cage is adjustable to admit different sizes of glass jars or test cylinders. Special cage designs can be built to customer's specifications. The standard model operates on 115 volts a.c. or d.c.; price $95, complete with four glass jars. **6**

Radiation Monitor

A new instrument that detects and records dangerous gamma radiations in an area and sounds an alarm when average tolerance limits are exceeded has been announced by General Electric Co. Called an area health monitor, the device provides an instantaneous indication of radiation, total radiation received in any preset period, and a 3-day integrated record of the radiation present in the immediate vicinity of the detector in 15-minute intervals. It also contains a means of telemetering the rate of radiation to remotely located indicating stations.

The new monitor is not meant to replace film badges or

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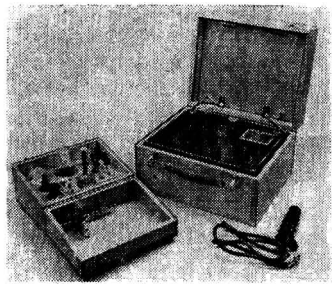
chambers carried by workers who frequent places where radioactivity is present, but rather to monitor whole areas. The standard equipment consists of an air wall ionization chamber, a d.c. amplifier, a 6-foot instrument panel that incorporates a torque-balance converter, a watt-hour-meter mechanism, a rate indicator, a cyclometer counter, and a recording device. Since the monitor uses an air equivalent ionization chamber as its primary source, it is not dependent upon the energy of the source. Its range is 0.5 to 5 times tolerance (tolerance is 6.25 mr. per hour), with an over-all accuracy of ±10%. The instrument employs a power supply of 115 volts, 60 cycles. **7**

Laboratory Reagents

Three laboratory reagents have been announced by the Fisher Scientific Co. Anthrone, C.P., important in carbohydrate detection, also figures in the estimation of serum polysaccharides. Sodium 2-naphthyl phosphate, C.P., is used in the colorimetric determination of acid and alkaline phosphatase. Silver iodate, now available in the tested purity grade, is one of the chief reagents employed in the clinical colorimetric determination of the chloride content of various body fluids. **8**

pH Meter

The new universal pH meter available from the Research and Control Instruments Division of North American Philips Co. is designed for pH work, potentiometric titrations, and oxidation-reduction potential measurements. The instrument provides a measuring accuracy of 0.01 pH or 0.5 mv. and a range of 0 to 14.15 pH and 0 to 1415 mv. It can be used with glass, quinhydrone, hydrogen, and platina electrodes and is directly calibrated for the first three.



The meter is supplied with removable calomel and glass electrodes and is provided with controls which correct for temperature variations and for asymmetric potentials. The unit has a built-in cadmium standard cell and a flexible cable with a plug for connection to a 60-cycle a.c. power source. Transformer taps can be changed to accommodate voltages of 110, 125, 145, 200, 220, and 245 volts. The meter is enclosed in a wood cabinet measuring 16.4 × 13.6 × 10.0 inches and weighing 46 pounds. An auxiliary chemical assembly in a wood cabinet, 11.5 × 8.6 × 7.5 inches and weighing 11.5 pounds, is available as an accessory. **9**

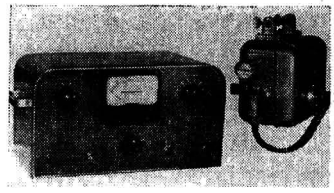
Monochromator

A new optical principle, permitting double monochromator performance with single monochromator simplicity, has been incorporated into the Model 99 double-pass monochromator now in production by the Perkin-Elmer Corp. The instrument may be used wherever a pure source of chopped monochromatic light is needed, such as in photometric chemical analyses and in medical or biological studies. In such applications, the instrument is said to provide the high efficiency of a double monochromator system at a cost comparable to that of a single monochromator.

Based on a simple method of reflecting radiation twice through the same optical system, the instrument provides the performance of a double monochromator of the same prism size and focal length with regard to dispersion, freedom from scattered radiation, and available energy. Model 99 is usable throughout the entire range of the ultraviolet, visible, and infrared regions of the spectrum (2000 A. to 40 microns) with suitable prisms. Resolution is better than 0.5 A. at 2500 A., and the scattered radiation is less than 0.1% throughout the entire range. The dimensions of the instrument are 14 × 14 × 9 inches. A wide variety of accessories, such as source units, detector mounts, and thermocouples, are available. **10**

Carbon Dioxide Analyzer

The carbon dioxide analyzer offered by Liston-Becker Instrument Co. is built in two sections: a pickup unit and an electronic section. The pickup unit measures 6 × 4.5 × 8 inches. Its absorption cell consists of a 0.75-inch inside diameter tube, 8 inches long. The total volume of the absorption cell is 47 ml., with approximately 30 ml. required to flush a sample from the entrance through the optical section of the absorption cell. The standard units are designed for 0 to 15% concentration full scale, with sufficient gain to make 0 to 5% full scale. Normally, the instrument is accurate to 0.2% carbon dioxide and can be made accurate to better than 0.1% if frequent calibration is employed. The response to nitrous oxide, ethyl ether, cyclopropane, water vapor in standard concentrations, and all the gases ordinarily found in the atmosphere is less than 1% full scale. Consequently, these interferences have negligible effect upon the accuracy of the instrument.



The electronic section of the analyzer measures 15 × 10 × 8 inches. In addition to its meter, the instrument has an output jack which can be attached to standard recorders. The instrument will give 90% response in 0.33 second when employed with a suitable recorder. **11**

Geiger Shield

A newly designed shield and mount for side-window glass Geiger tubes, designed to eliminate the unsatisfactory features of previously available models, is announced by Nuclear Instrument and Chemical Corp. The Model 3030A shield is arranged for the mounting of a glass Geiger tube horizontally and for the placement of a sample close to this tube surrounded by 2.5 inches of iron for background shielding purposes. This shield will accept many sizes of sample holders and incorporates a means of counting in three accurately predetermined geometries. Absorbers may also be used when desired. **12**

Electronic Microcomparator

Graham-Mintel Instrument Co. reports the availability of a new electronic microcomparator, an instrument which reads directly in millionths of an inch. The instrument consists of an induction-type gage head adjustably mounted on a rigid stand, and a high-stability four-tube amplifier with a two-scale meter. The gage head has a frictionless movement, with no mechanical amplification. The amplifier is free of drift, and readings are not affected by any ordinary fluctuations in line voltage or by nearby magnetic fields. Consistent readings are obtained on both continuous and intermittent use.

The meter has two continuous linear scales which read 0.000001 and 0.000010 inch per division, either side of zero. The scales can be used interchangeably at will. Meter responses are instantaneous, permitting fast and dependable readings.

The work is placed on an anvil mounted in a holder on the base of the stand, with the anvil either parallel or at right angles to the front of the base. The gage head is positioned by a rack-and-pinion vertical adjustment and accommodates work of any height up to 12.5 inches above the top of standard anvils. Fine adjustment is provided by a knob on the

gage head (0.0035 inch per turn). To facilitate the placement of the work in the measuring position, a push button at the front of the base works through a cable to raise the contact tip about 0.003 inch. Other features of the instrument include a 4-ounce contact pressure and a replaceable contact tip with overtravel protection. **13**

Sequestering Agent

A new sequestering agent, 2-thenoyltrifluoroacetone, is being manufactured and sold in limited quantities by the Dow Chemical Co. This compound has the property of forming complex molecules with various metallic ions in solution. The use of the material permits the separation of ions which are ordinarily difficult to separate chemically, since small adjustments in pH cause pronounced changes in the amount of complexing. The product is priced at $30 a pound in 1-pound lots. **14**

MANUFACTURERS' LITERATURE

Surface-Active Agent. Bulletin describes chemical and physical properties of surface-active agent, sodium alkyl naphthalene sulfonate. Solubilizing, foaming, emulsifying, wetting, and biological properties are covered. Product may be used in textile industry, metal processing, polymerization, and fire control. Alrose Chemical Co. **15**

Pyrometers Bulletin 1051 discusses indicating pyrometers, resistance thermometers. Circuit and engineering diagrams are included. Minneapolis-Honeywell Regulator Co. **16**

Laboratory Equipment. Latest issue of *Laboratory Specials* features Beckman Model B flame spectrophotometer, wrist-action shakers for flasks, polyethylene wash bottles, and neoprene matting that protects sink and table tops. A. S. Aloe Co. **17**

Organic Chemicals. Catalog covers prices of 34 organic chemicals available in laboratory, pilot, and commercial quantities. Terms and services are fully described. Arapahoe Chemicals, Inc. **18**

Herbicide. A hormone-type weed killer, 2-methyl-4-chlorophenoxyacetic acid, is subject of bulletin that describes product's properties and uses. Bulletin contains a list of weeds classified according to their susceptibility to compound. Monsanto Chemical Co. **19**

Triallyl Cyanurate. A 12-page booklet discusses physical and chemical properties, potential applications, and toxicity of triallyl cyanurate. A bibliography is included. American Cyanamid Co. **20**

Servomechanisms. Servomechanisms, discussed in 24-page booklet, offer a new tool for improved process control and more economical process design. Booklet provides basic information on this new approach to the analysis of automatic control problems in industrial instrumentation. Minneapolis-Honeywell Regulator Co. **21**

Dynel Clothing. Pamphlet discusses Dynel work clothing, which resists acids, alkalies, wear, moths, mildew, shrinkage, and tearing. Available as shirts, trousers, and coveralls, garments offer excellent protection, are comfortable, and neat in appearance. Mine Safety Appliances Co. **22**

Laboratory Apparatus. A 16-page booklet, "What's New for the Laboratory," describes latest assortment of laboratory apparatus, including stirrers, balances, absorption cells, pumps, manometers, centrifuges, and pH meters. Scientific Glass Apparatus Co. **23**

Spectroscopy. Latest issue of *Announcer* contains historical discussion of chemical spectroscopy. Company's equipment, such as manometer calibrator, hot plates, clinical shakers, bottle and drum tilters, biological incubators, and automatic titrators, is described. Eberbach and Son Co. **24**

Surface-Active Agents. A 16-page booklet describes three new esters of sodium sulfosuccinic acid (butyloctyl, tridecyl, and *tert*-butylphenoxyethyl). Information is given on physical, chemical, and surface-active properties, as well as on potential applications and toxicity. American Cyanamid Co. **25**

Fatty Alcohols. Bulletin provides information on compounds such as cetyl, oleyl, and stearyl alcohols and describes their typical uses in chemical processing industry. M. Michel and Co. **26**

Carboxymethylcellulose. Physical and chemical properties of product, as well as major applications, are discussed in technical booklet. Details on types of CMC available, viscosity, compatibility, and other pertinent data are given. Hercules Powder Co. **27**

Chemicals. A 52-page catalog describes company's botanical drugs, chemicals, insecticide concentrates, and rodenticides. Also described are the company's processing and manufacturing facilities, foreign representation, and research organization. Prentiss Drug and Chemical Co. **28**

Abrasion Tester. Brochure describes Model 140 abrasion testing set, as well as several new types of specimen holders. Taber Instrument Corp. **29**

Sodium. A 24-page illustrated booklet, "Handling Metallic Sodium," discusses the safe handling of sodium from 1-pound bricks to 80,000-pound tank cars. Physical and chemical properties of sodium and a bibliography are included. National Distillers Chemical Corp. **30**

pH Indicator Chart. New pH indicator chart shows hydrogen-ion concentration ranges and color changes of company's indicators and gives directions for the preparation of indicator solutions. Eastman Kodak Co. **31**

Diffusion Pumps. Bulletin describes and charts the characteristics of Type MCF diffusion pumps. These all-metal fractionating pumps are recommended for the evacuation of equipment requiring an ultimate pressure of less than 10^{-5} mm. of Hg. The pumps range in size from a 2-inch diameter model suitable for the exhausting of cathode-ray tubes to pumps several feet in diameter used on synchrocyclotrons and linear accelerators. Bulletin provides information on forevacuum, fractionation, speed, baffles, and installation of pumps. Distillation Products Industries. **32**

Scientific Instruments. Booklet describes and illustrates the important features of some 20 different instruments and accessory units, including pH meters, glass electrodes, spectrophotometric equipment, flame attachments, automatic titrators, colorimeters, and radioactivity instruments. Beckman Instruments, Inc. **33**

Unsaturated Silanes. Information on physical properties, typical reactions, applications, and availability of both vinyltrichlorosilane and vinyltriethoxysilane is presented in technical data sheet. Compounds are unique among currently available silicon chemicals because of their dual reactivity: reactions through the vinyl double bond and formation of polysiloxanes from the silane radical. Linde Air Products Co. **34**

Protective Coatings. A 24-page booklet discusses company's protective coatings for metal surfaces. Describing hot-application enamels, primers, and coupling compounds and cold-application enamels and bituminous paints, the booklet outlines the properties, uses, containers, performance tests, and application procedure for these coatings. Reilly Tar and Chemical Corp. **35**

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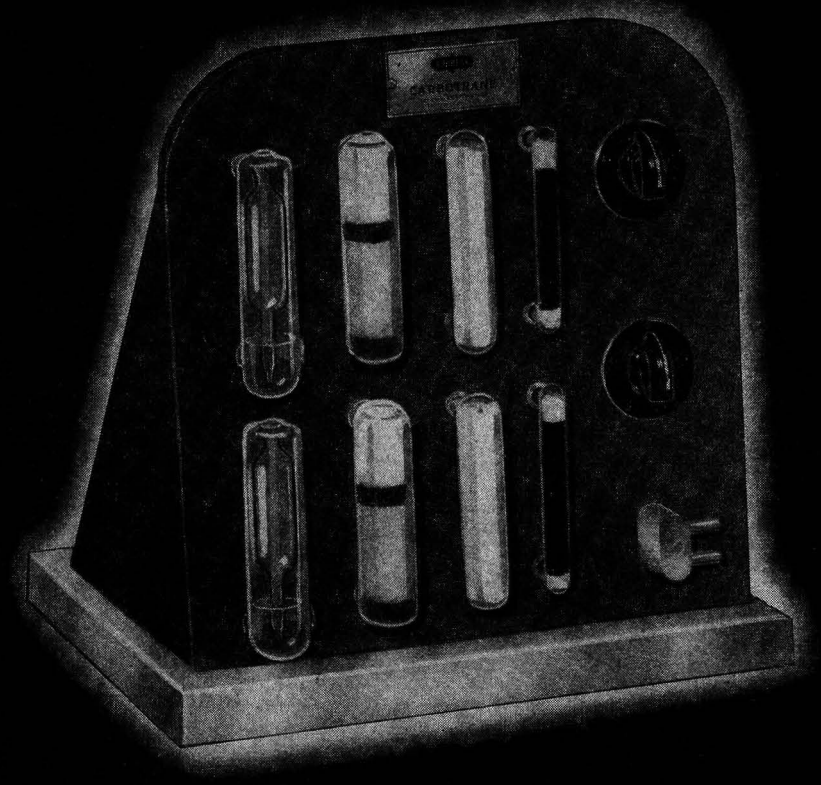

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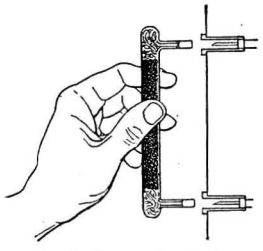

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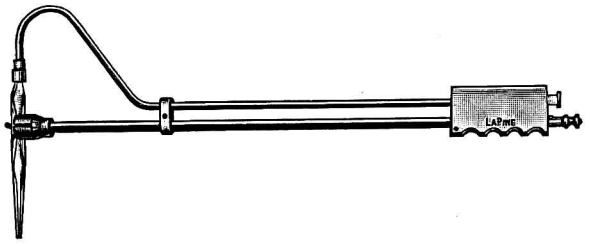

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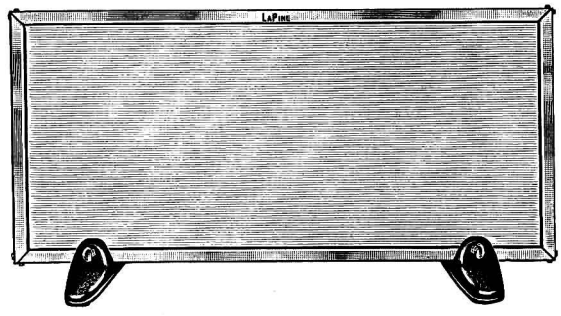

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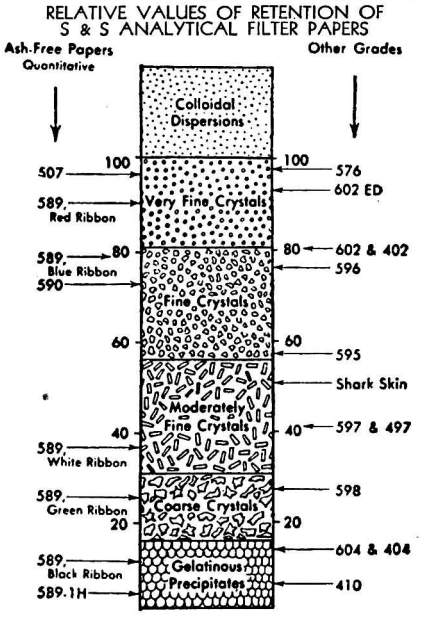

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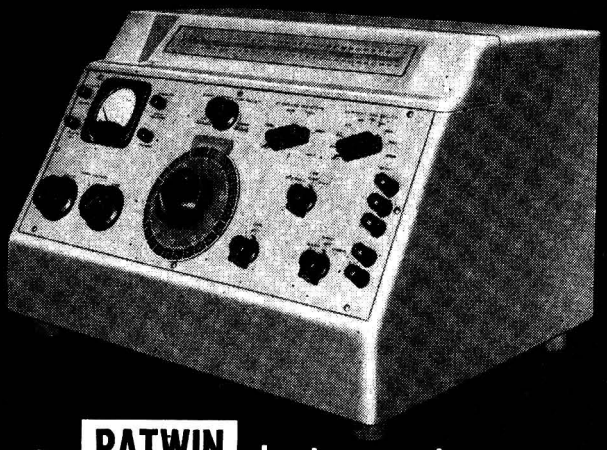

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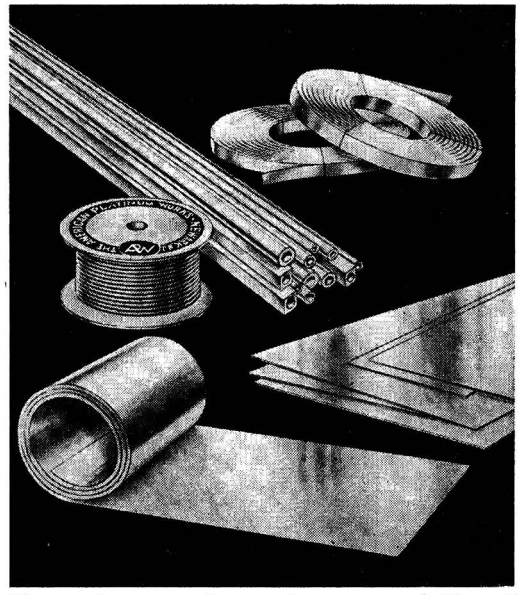

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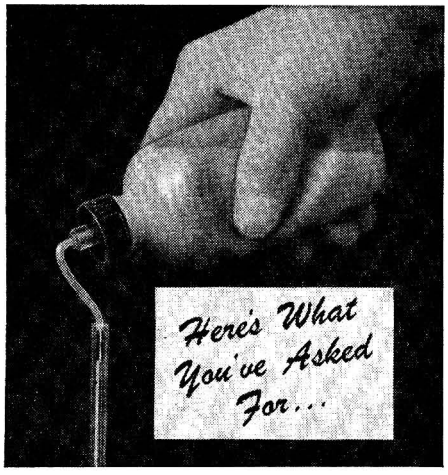

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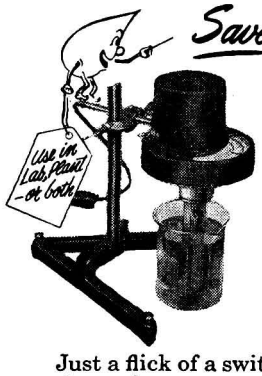

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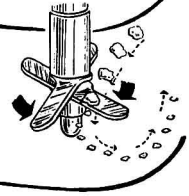

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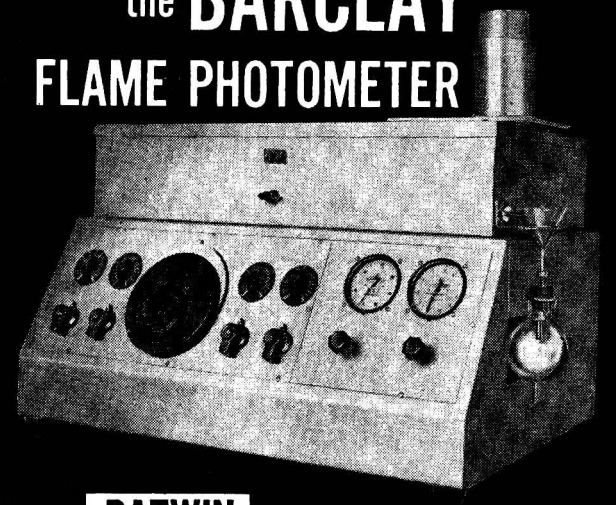

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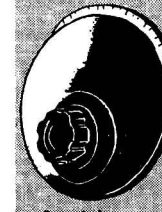
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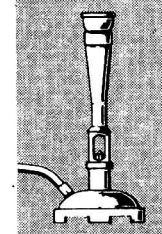
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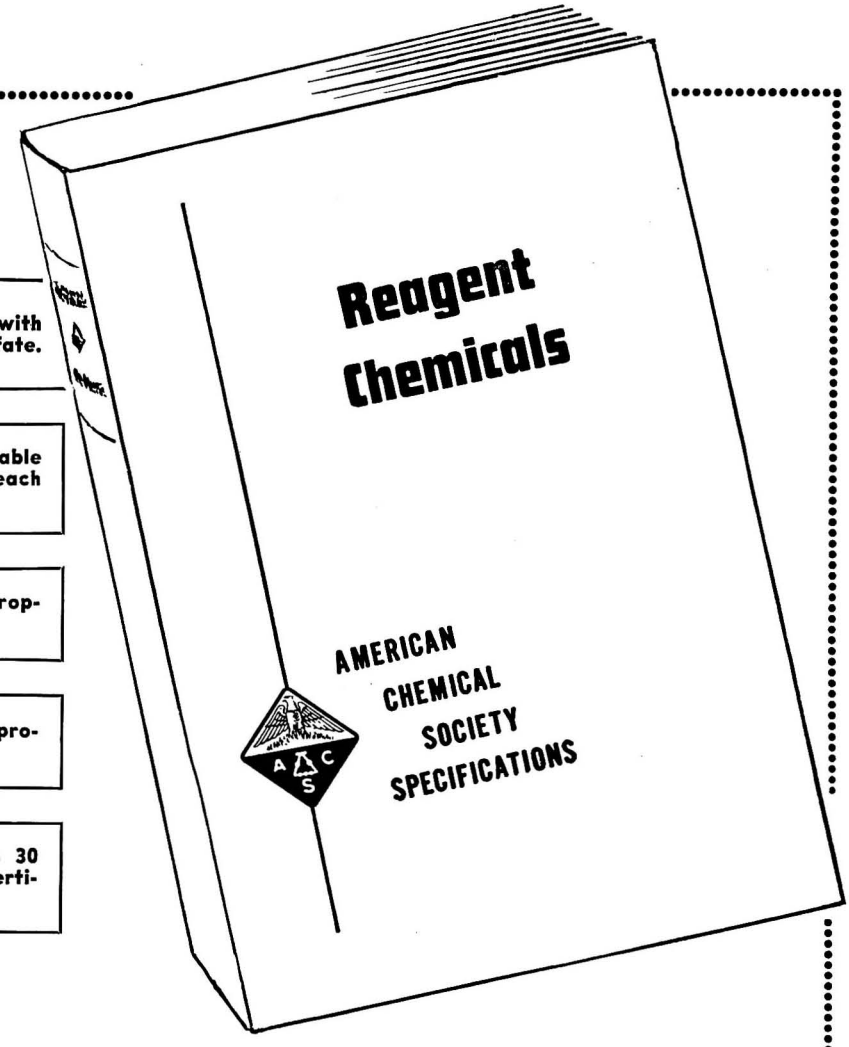

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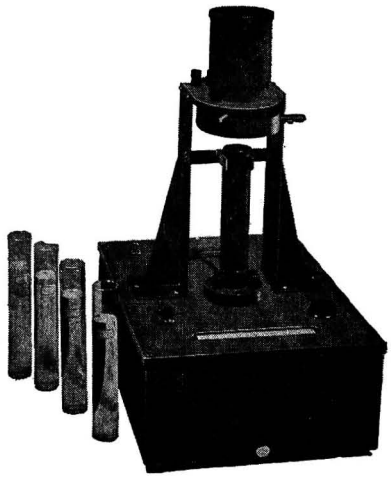

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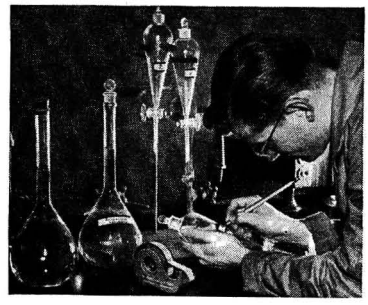

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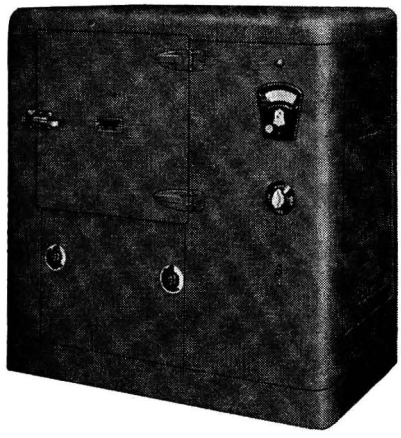

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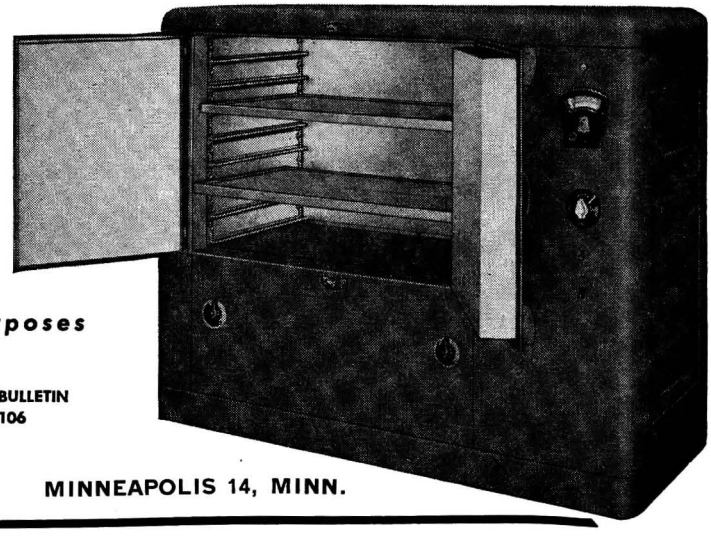

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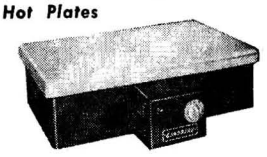

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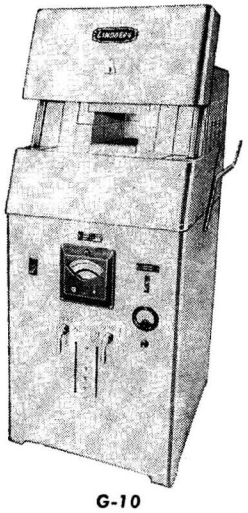

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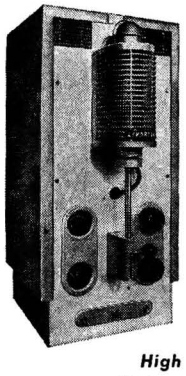

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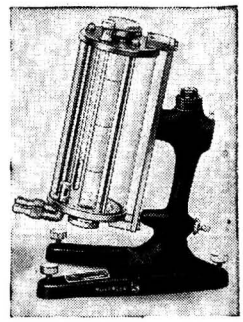

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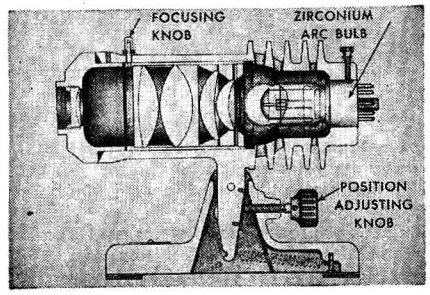

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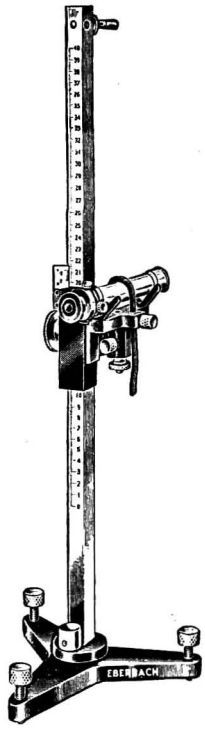

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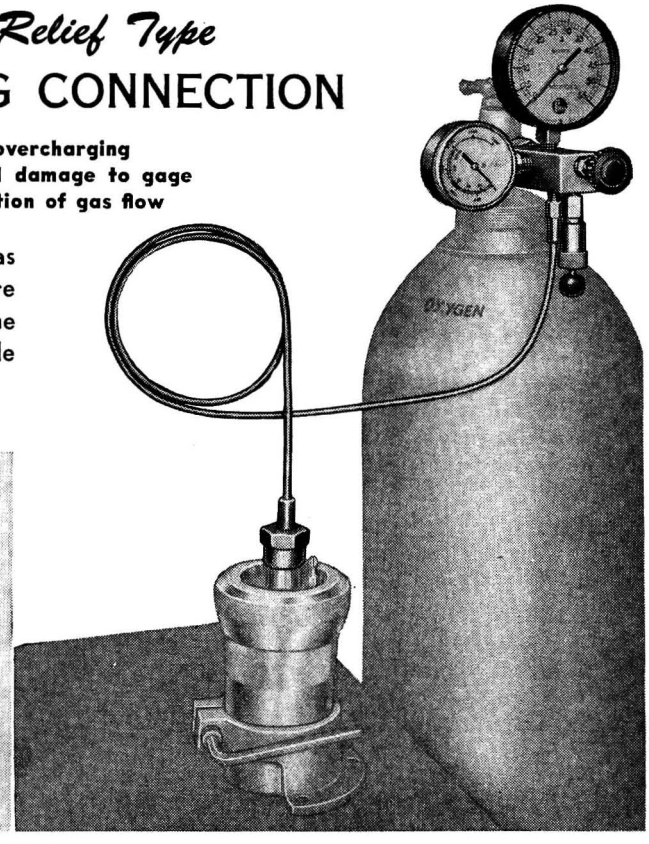

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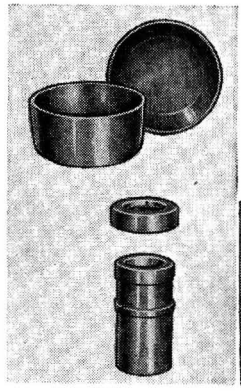

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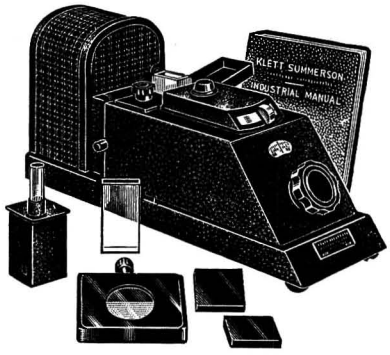

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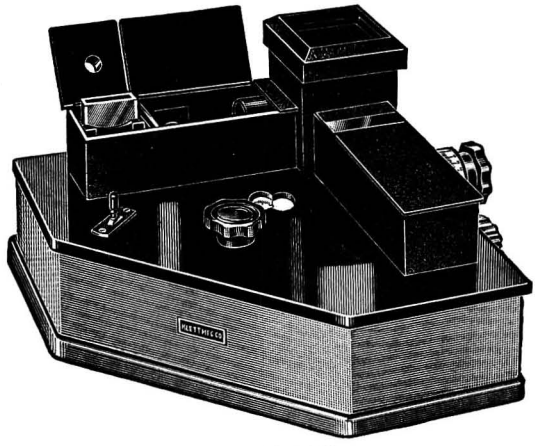

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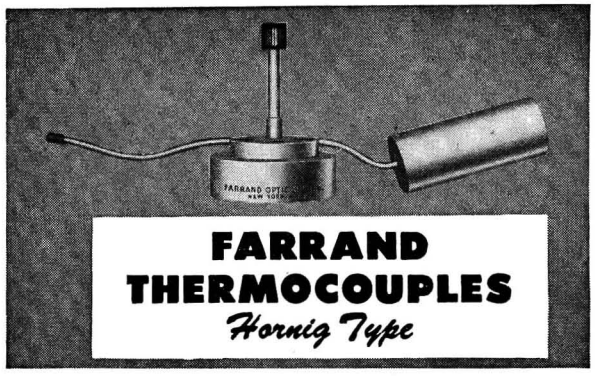

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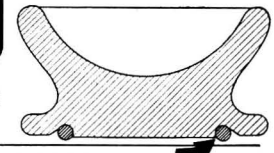

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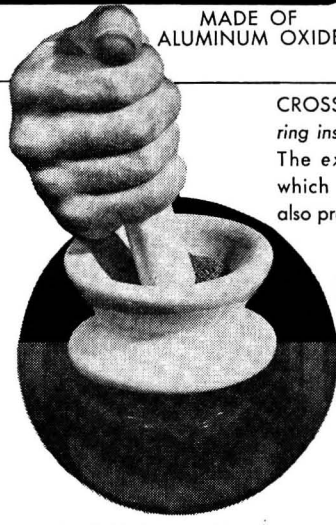

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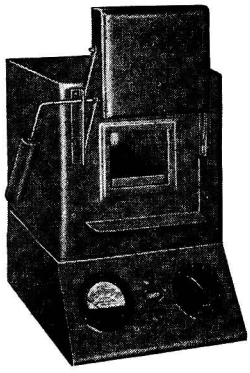

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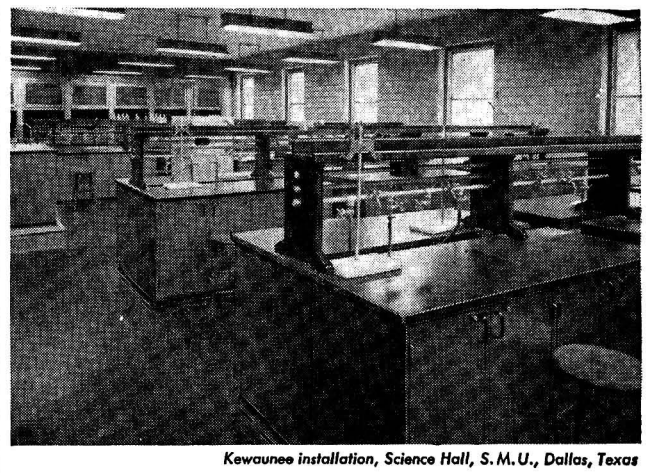

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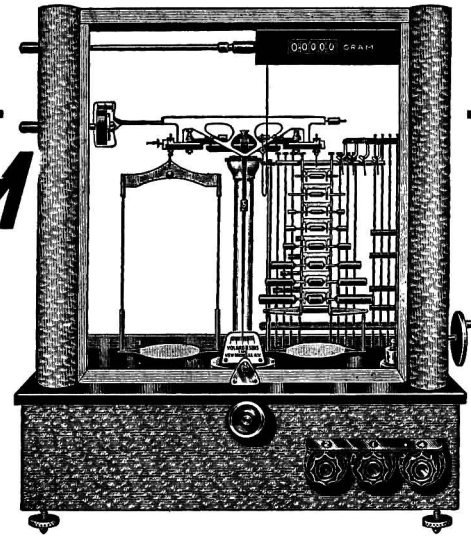

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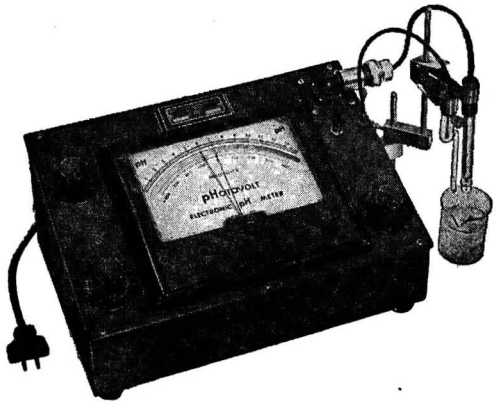

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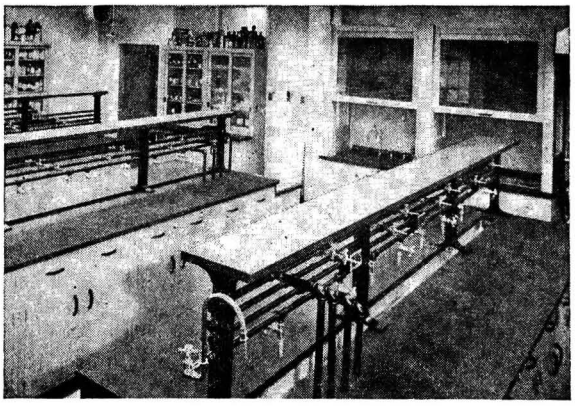

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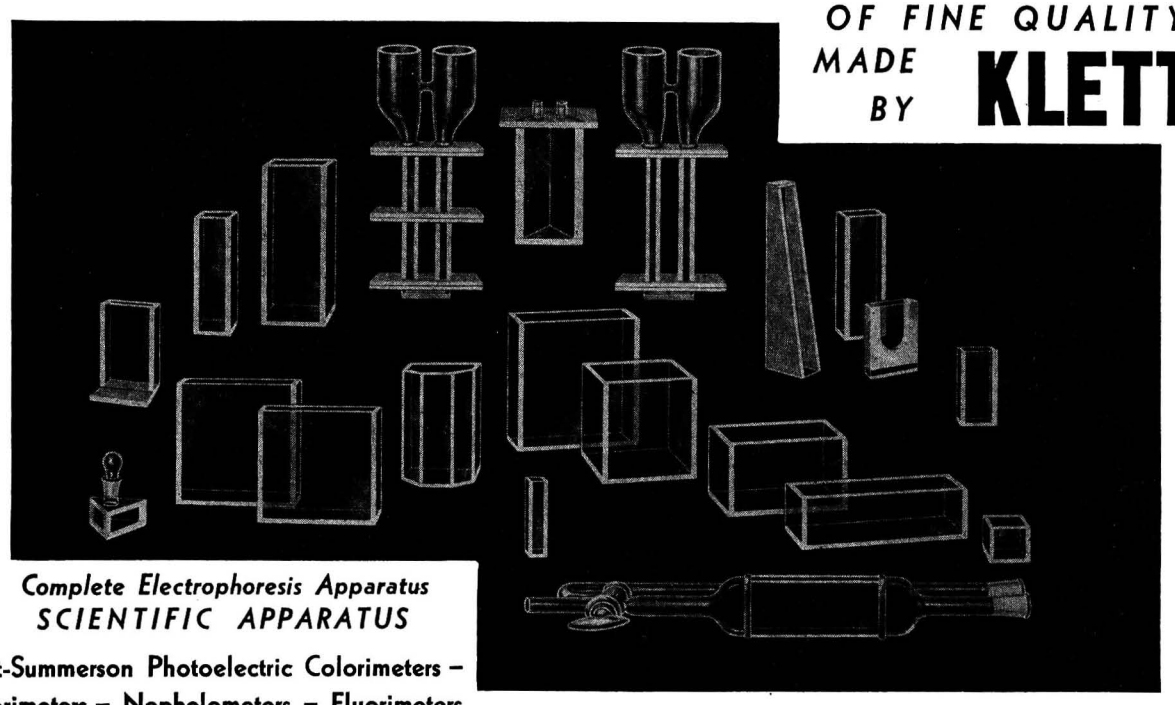

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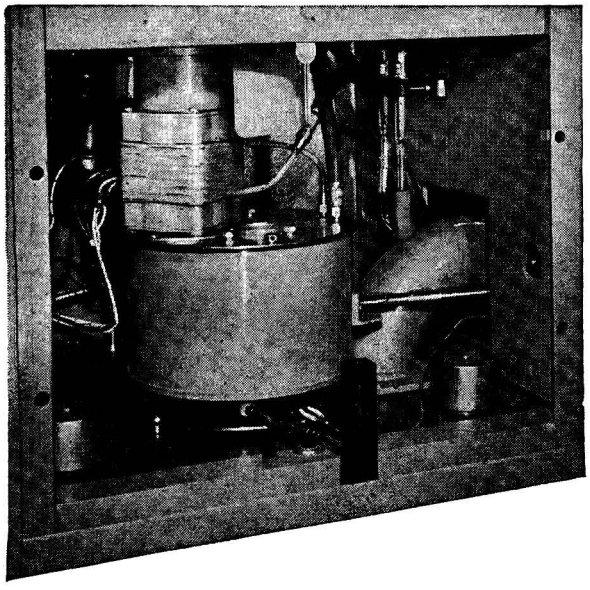

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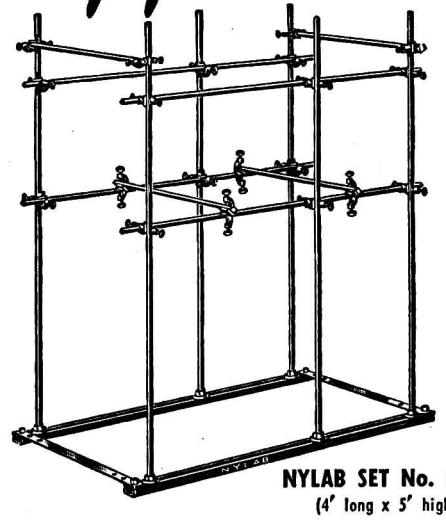

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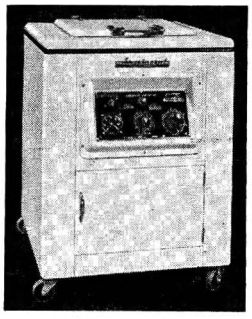

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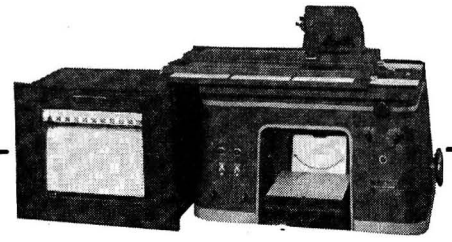

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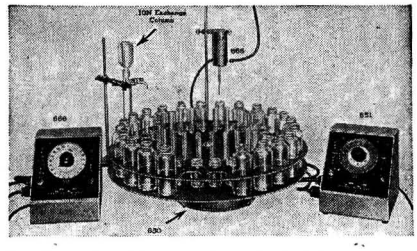

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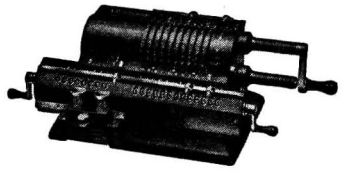

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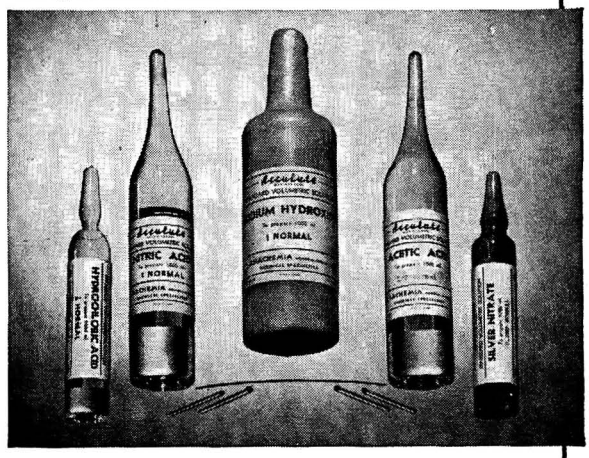

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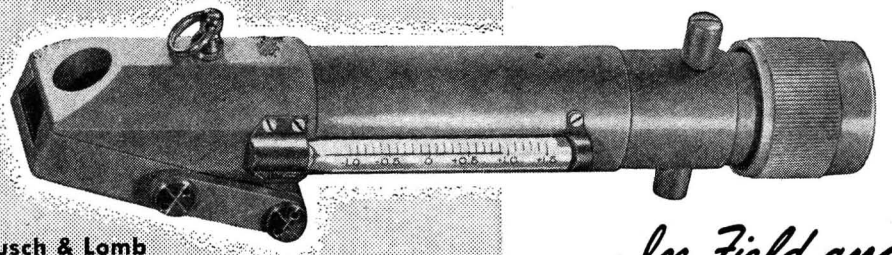

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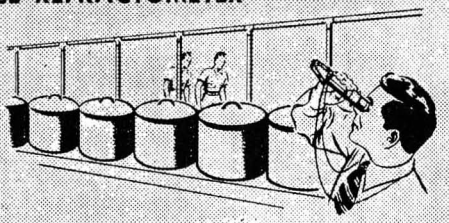

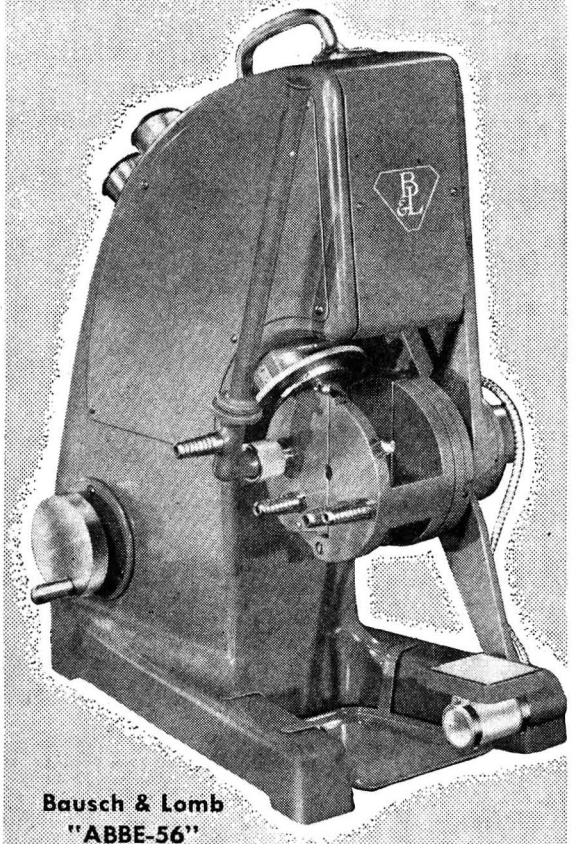

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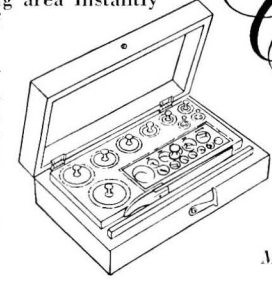

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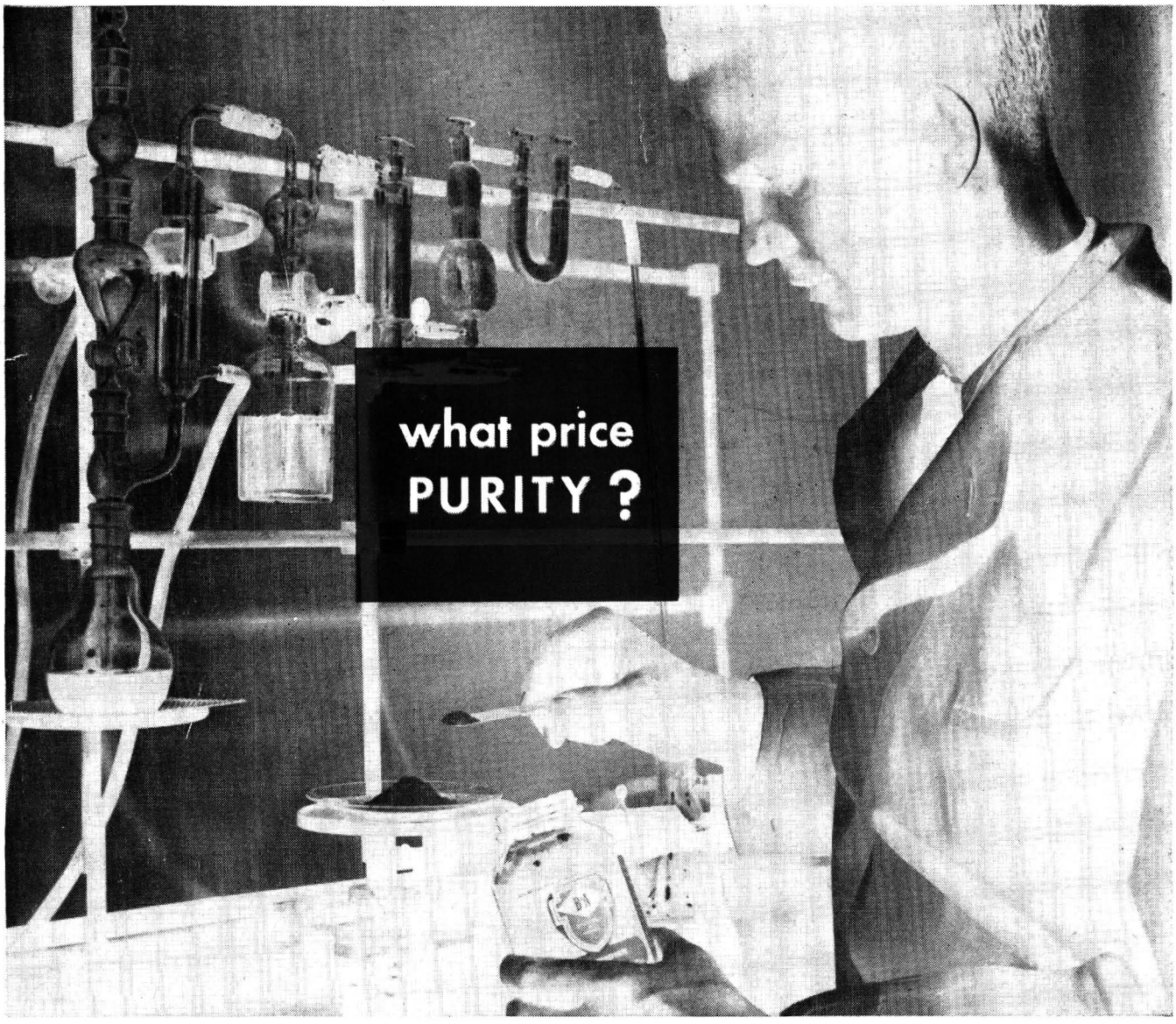

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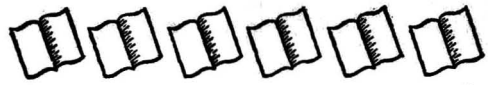

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