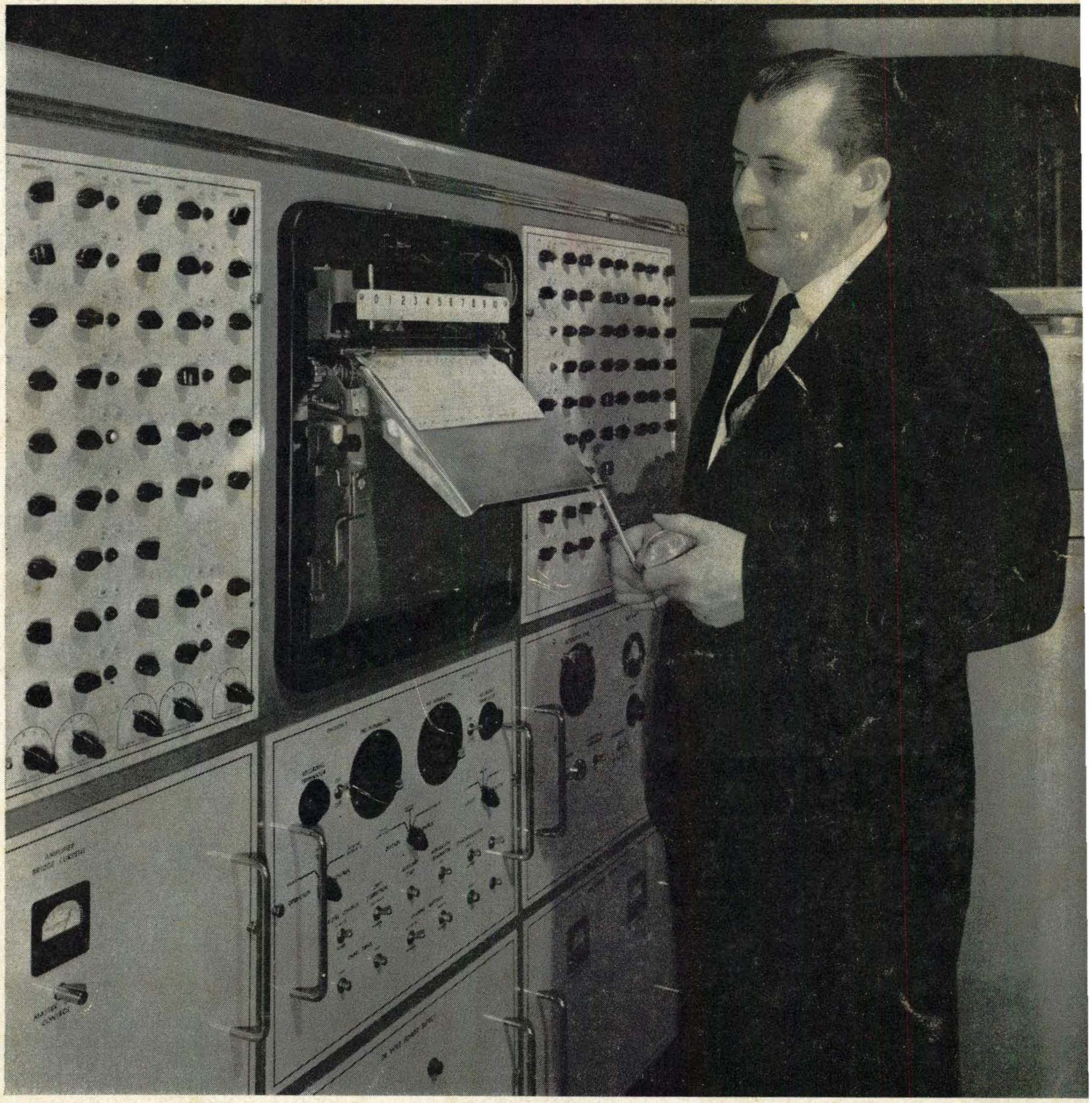
FEBRUARY 1952

ANALYTICAL CHEMISTRY

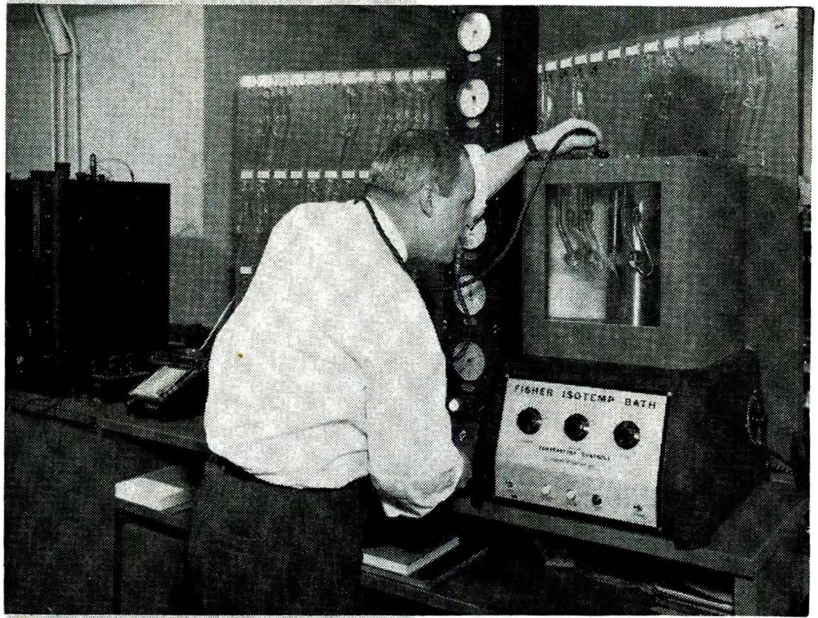


The direct reading spectrograph, already firmly established in aluminum industry, promises to revolutionize metallurgical control analysis

For Constant Temperature...

the FISHER
ISOTEMP BATH

offers all
6 advantag



1. Precise temperature control—to better than ± 0.005°C
2. Chatterproof resistors, thermocouples and relays
3. 400-watt control heater and 800-watt auxiliary heater
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5. Unobstructed top for free and easy access to the Bath
6. Wide range, −5 to +107°C

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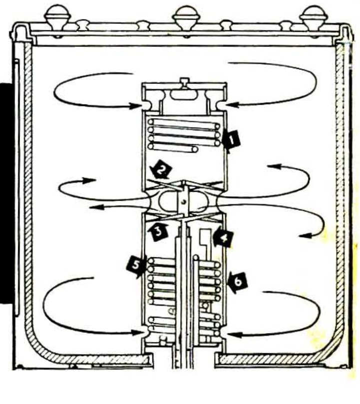
The Fisher Isotemp Bath introduces a new concept of precision, constant-temperature baths to meet the requirements of modern laboratory practice. Every feature — from its "coarse," "medium" and "fine" temperature adjustments to its virtually shadowless illumination — is included to facilitate the instrument's convenient operation and its precise control.

Write Today

An illustrated booklet describing these and other features of the new Isotemp Bath is now available. There is no obligation.

Within the new Fisher Isotemp Bath the cooling coil (1), counter thrust impellers (2 and 3), sensitive control element (4) and heater coils (5)—are all contained in central housing (6) to provide ample working space and free access to the Bath.



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ANALYTICAL CHEMISTRY

Volume 24, No. 2

Issued February 18, 1952

This Month's Cover. A new high in automatic analysis of alloys has been achieved in laboratories of Aluminum Company of America with the use of quantometers and other direct reading spectroscopic instruments. Alcoa's J. R. Churchill, shown operating a production control quantometer, is one of the leaders of analytical revolution in which analyses of historical import are being replaced by on-the-spot analyses to permit continuous control during metallurgical processes. About 70% of determinations made in Alcoa's plants are handled by direct reading instruments. The one in the photograph automatically produces a written analytical report within two minutes of presenting the sample and will handle all determinations normally required commercially on aluminum alloys.

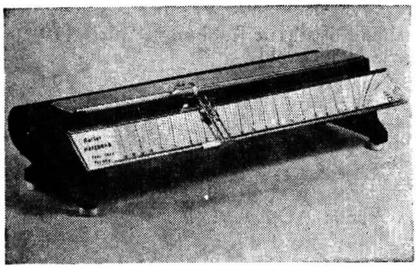
FOURTH ANNUAL REVIEW OF ANALYTICAL CHEMISTRY

Applications of Analytical Developments

(End of Review Section)

TITRATIONS IN NONAQUEOUS SOLUTIONS

(Continued on page 4 A)



CONTENTS, continued

MICROCHEMISTRY

NOTES ON ANALYTICAL PROCEDURES

CRYSTALLOGRAPHIC DATA

AIDS FOR THE ANALYST

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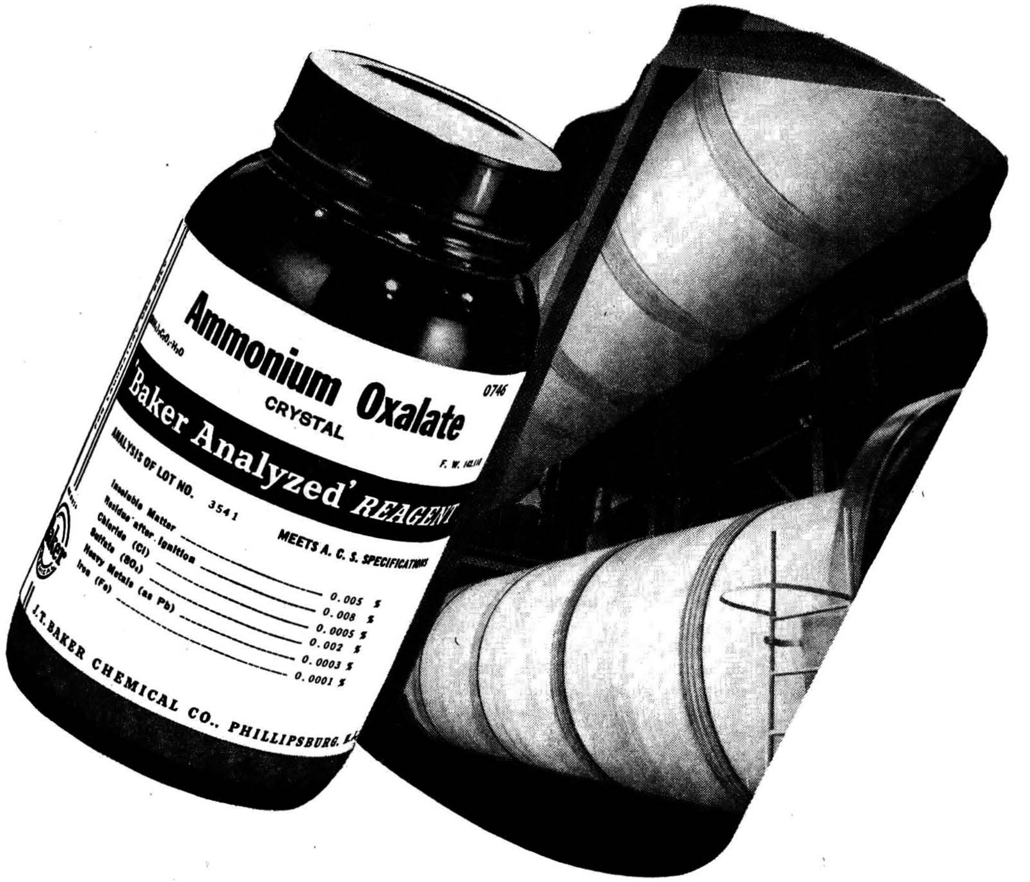
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Residue after Ignition 0.008 %
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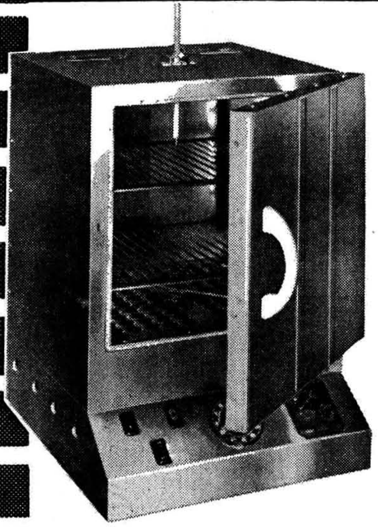

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Gravity Convection

● ruggedly constructed, versatile, dependable ● Army-Navy approved ● 1 cubic ft. cap. ● polished stainless steel 18-8, inside and out ● Fiberglas insulation 2″ thick ● temperature range 37 8° C. to 232° C. (100° F. to 450° F.) ● automatic hydraulic control, sensitivity ± ½° C.

● Modella heating element fully guaranteed; withstands 2600° F. ● wiring enclosed ready for instant service ● inside dimensions 12″ x 12″ x 12″ ● also available in other sizes ● automatic timer optional. **ONE YEAR GUARANTEE**

Model OV-460

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● large capacity, moderate price ● baked aluminum interior enameled grey exterior ● automatic 6 hour timer to control heat periods (optional) ● various sizes available
Dual Bank of Modella Heaters
GUARANTEED 2 YEARS

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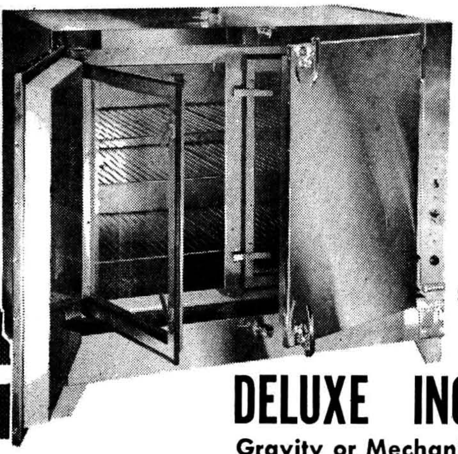
AND INCUBATORS



Series "INW"

DELUXE INCUBATORS

Gravity or Mechanical Convection

Wet Type ● Dry Type ● temperature range; room to 70° C.; constant ± ½° C. ● constructed to Army-Navy specifications ● Modella elements ● stainless steel 18-8 ● polished chrome hardware ● inner glass observation doors ● exclusive sealing design eliminates center mullion on largest size ● air velocity controlled from 25 f.p.m. to 150 f.p.m.

heating unit and control **four sizes ● two styles**
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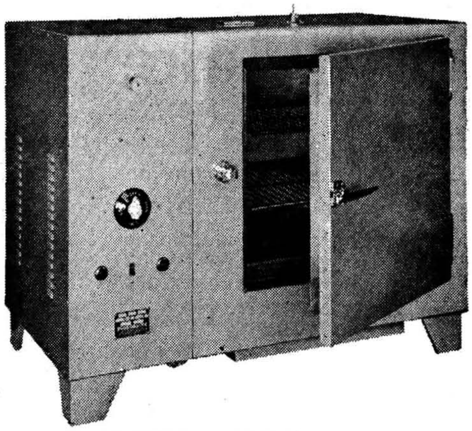

DELUXE UTILITY OVENS

Mechanical Convection

Bench or Table Styles ● Streamlined construction ● stainless steel interiors ● temperature ranges: 35° C. to 180° C. or 35° C. to 288° C. ● symmetrical heating ● horizontal airflow for constant temperatures ● power selector switch ● wattage control speeds work ● controlled velocity

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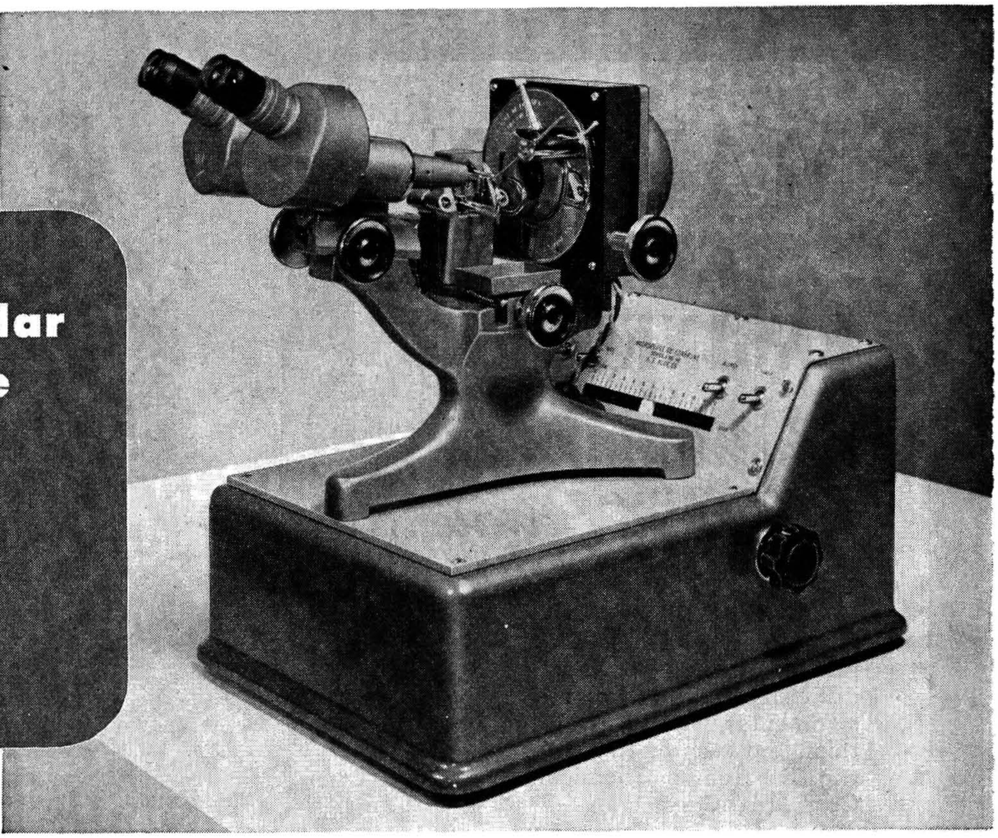
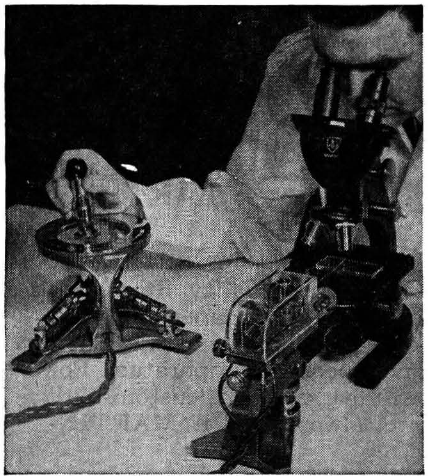


New Binocular de Fonbrune Micro-forge

Extends potential application of any micromanipulator

Micro-probes, scalpels, needles and other tools made to exact specifications under controlled conditions



de Fonbrune Micromanipulator

Uniform pneumatic movement

The de Fonbrune micromanipulator, manufactured under exclusive license to the French patents, affords new simplicity and flexibility in micro-studies. It is equally suitable for biological or clinical technics. The micromanipulator consists of a manipulator and receiver. These units may be used with any type of microscope . . . arranged for right- or left-hand operation. Within a range of 3 mm, the micro-tool is moved in any plane or direction by a single control lever. Ratio of displacement between lever and micro-tool may be adjusted from 1:50 to 1:2,500.

The improved de Fonbrune micro-forge with stereoscopic microscope is an indispensable accessory for all types of micromanipulators. With this convenient micro-forge, micro-pipettes, micro-scalpels and numerous other micro-instruments are fabricated under accurately controlled conditions. Only little practice is necessary for an investigator to acquire skill in manipulating the various controls in manufacturing micro-tools. Ready availability of standard and special micro-tools often proves of genuine advantage in utilizing the full potentialities of the micromanipulator in both routine and special studies.

Binocular body provides three dimensional vision

The micro-forge is basically a combination of optical and electric forge units. In the improved model, the optical system includes a microscope with inclined binocular body in place of the monocular type. This stereoscopic microscope not only provides three dimensional vision but also shows the image erect. The microscope is equipped with 4X paired objectives and 9X paired wide field eyepieces. These optics provide a magnification of 36X with a large working field. The electrical forge is mounted on an adjustable stage directly in front of the microscope objectives. Two insulated clamps support the cylindrical electrodes connected by a platinum-iridium filament providing temperatures from about 120°F. to 3000°F. Air jets are also mounted on the stage. The lamp housing is set opposite the objective and forge unit. A pivoting spindle for supporting the material is mounted at the periphery of a disc in front of the lamp housing. Both spindle and disc may be rotated about their own axis and the entire assembly adjusted vertically or horizontally. Controls are provided for adjusting the light to the objective. A detailed manual of instructions is furnished with each micro-forge. Accessory equipment including the air pump, rheostats, and transformer is contained in the base. The entire unit is finished in baked-on gray enamel.

Write for prices and descriptive bulletin T114

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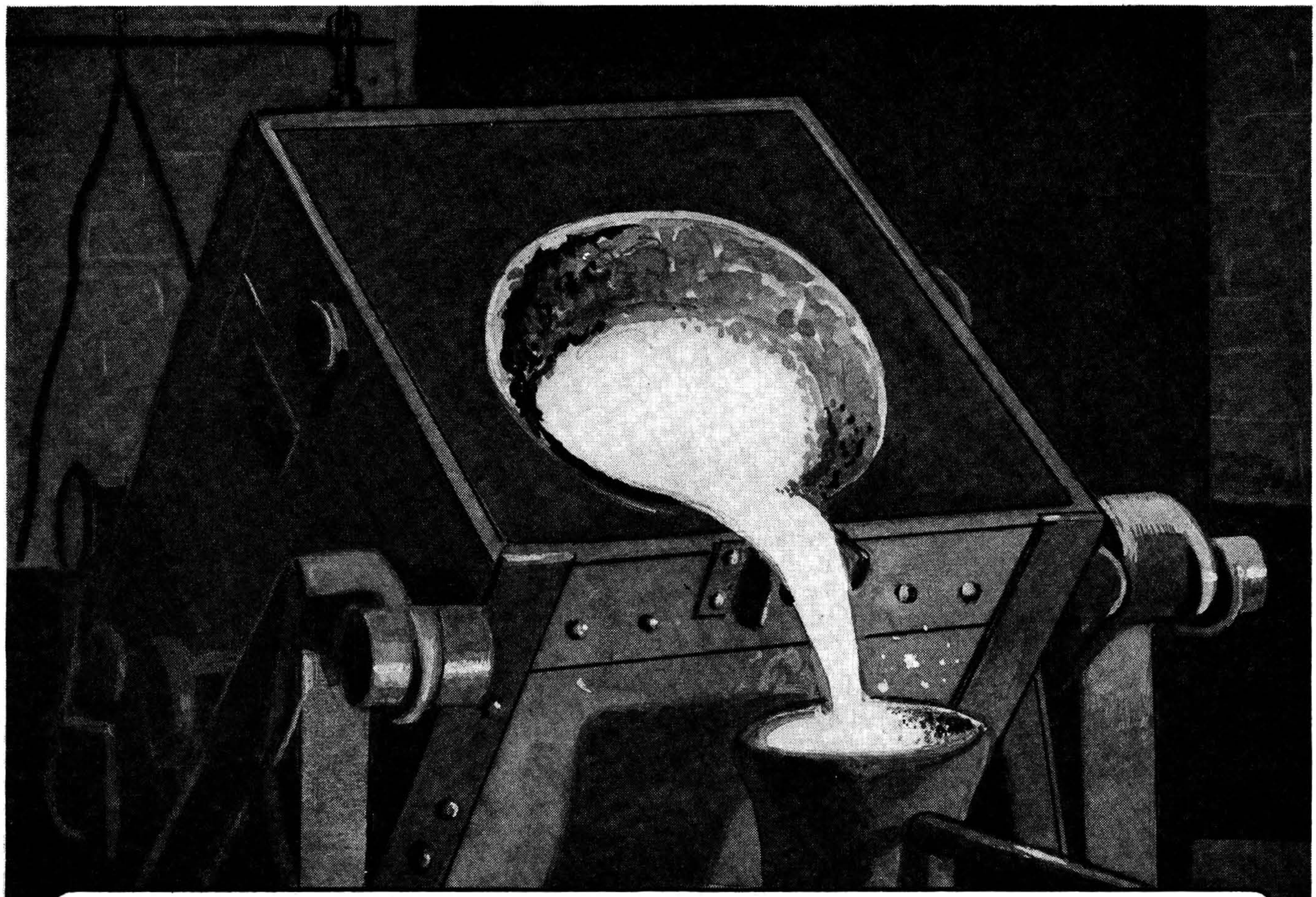
UNUSUAL APPLICATIONS OF SPECTROGRAPHIC ANALYSIS...



CONTROLLING "NICHROME"* FURNACES IN DRIVER-HARRIS FOUNDRY...

Driver-Harris Company's famous "Nichrome" and "Nichrome" V — leading alloys, used as heating elements in all sorts of products from common toasters to high-temperature electric furnaces — are rigidly controlled from the foundry to the finished wire by spectrographic analysis.

In addition to "Nichrome", Driver-Harris depends upon the spectrograph to maintain the extremely high standard of many other alloys ... to speed up operations ... to hold analysis costs down. They use "National" spectroscopic electrodes.

Why it pays to use "National" spectroscopic electrodes. National Carbon's spectroscopic electrodes are the purest obtainable. Each shipment is accompanied by a "Statement of Purity" which tells your analyst what trace elements are present in the electrodes. As a result, he can assess his plates or film very quickly and accurately without being confused by unexpected spectral lines.

*Registered trade-mark of D-H Company

OTHER ADVANTAGES OF SPECTROGRAPHIC ANALYSIS

- Sensitive to 1/10,000,000 of a gram for some elements
- Saves time in analysis
- Detects unsuspected metals
- Accurate testing is possible with very small sample
- Provides a permanent record
- Differentiates between two elements chemically very similar
- Analysis can be made in some cases without destroying sample

The term "National" is a registered trade-mark of Union Carbide and Carbon Corporation

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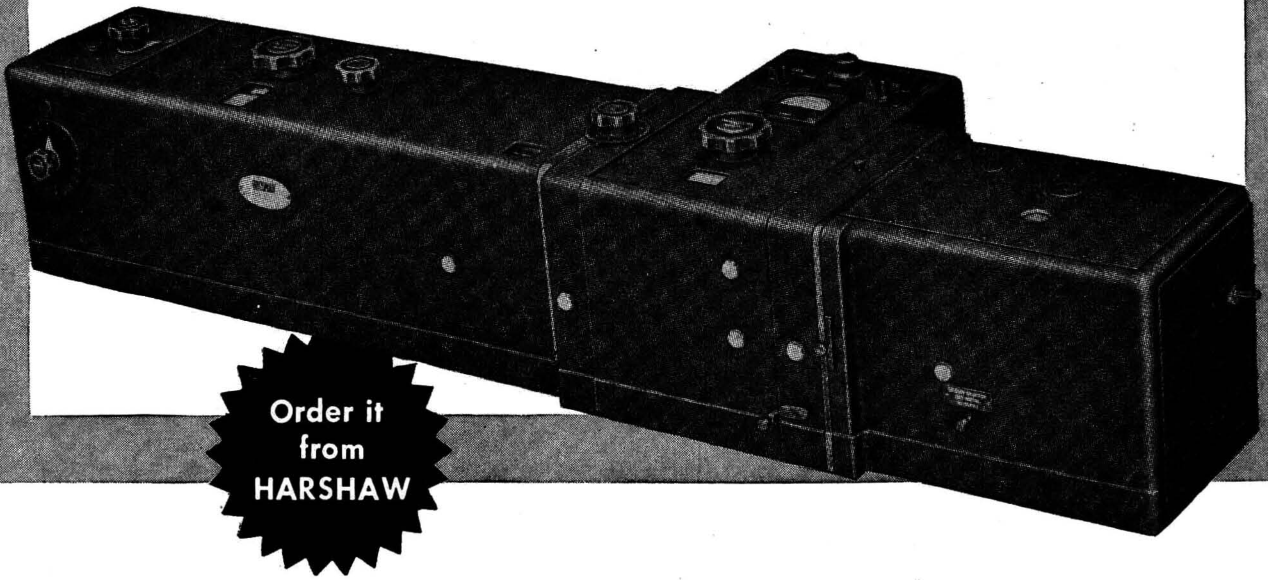
BECKMAN *Model* IR-2
Infrared Spectrophotometer



The Model IR-2 Infrared Spectrophotometer is unsurpassed for accuracy, convenience, and overall usefulness in research investigations, analytical laboratory determinations and for the continuous automatic control of plant streams.

Many design features contribute to the convenience and speed of operation of the IR-2: Elimination of zero drift and non-linearity through the use of chopped radiation and an a-c amplifier; minimized stray energy by advanced optical design and employment of a filter-beam chopper; construction in separate compartments, making the IR-2 the most adaptable instrument available; Incorporation of a turret-stop mechanism for quick, accurate setting to predetermined wave lengths; collimation of the radiation beam so that the focus is unaffected by substituting special cells of various lengths; direct calibration of the monochromator in wavelength units to eliminate conversion charts; dual gas cells independently filled and positioned without removal from their compartment.

The Beckman Model IR-2 excells in performance: precise reproducibility of transmission measurements; high resolution of better than 3 cm^{-1} at 10 microns; reduction of stray light to less than 1 per cent at 14 microns and to less than 2 per cent at 15 microns; excellent reproducibility of slit and wavelength settings; constant energy output of the source; linear detecting and amplyfying system not subject to uncontrolled fluctuation in sensitivity.

The instrument's fundamental design is similar to that which has proven so successful in the well-known Beckman Model DU Quartz Spectrophotometer. The model IR-2 is constructed of separate units which are easily assembled and disassembled. A rugged, sealed monochromator mounted in a steel housing is the principal unit. To this are attached three other units in the standard instrument; the light-source compartment, the gas-cell and energy receiver compartment, and the liquid-cell compartment. Because other units such as special radiation sources or receivers, or different cells and cell compartments can be attached as desired, the instrument is readily adaptable to specialized measurements and to the changing requirements of research and plant control.

MODEL IR-2S SPECTROPHOTOMETER. Comprised of three units; the instrument assembly with sodium chloride optics, the electronic amplifier, and the power supply for use on 115-volts, 60-cycles. The instrument is assembled with monochromator and three integrally attached units: the energy receiver compartment with thermocouple, the liquid cell compartment, and the light source compartment with phototube regulator, beam chopper and auxiliary metal fixed gas cell, approx. 27-cm. Other cells listed separately. Direct reading wavelength scale 1.0 to 15.0 microns. Shipping weight 400 lbs. **$4650.00**

Contact Harshaw for all Beckman Instruments

See this instrument demonstrated in Booths 18-19, March 5-6-7, 1952 at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy. Wm. Penn Hotel, Pittsburgh, Pa.

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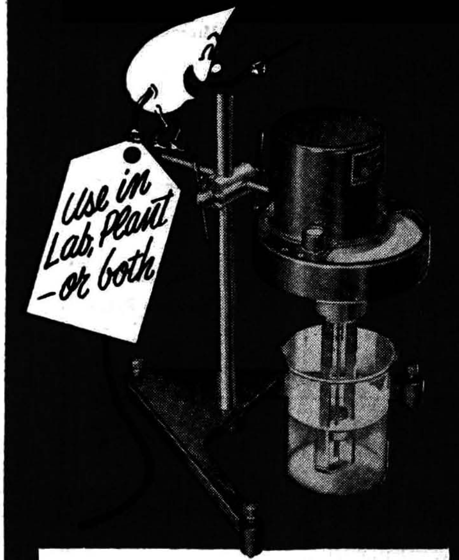
VISCOSITY DETERMINATION AND CONTROL



Made as Easy as . . .

Just a flick of a switch, then read the dial, and with a Brookfield Synchro-Lectric Viscometer on the job you have your viscosity determination in centipoises. The whole operation, including cleaning up, usually takes only a minute or two.

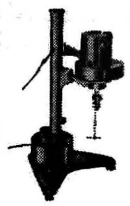
Available in a variety of models* suitable for extremely accurate work with both Newtonian and non-Newtonian materials, Brookfield Viscometers are portable and plug into any A.C. outlet —can be used in Lab, Plant or both.

Write today for fully illustrated catalog showing Brookfield Viscometers and accessory equipment adaptable to any viscosity problem from less than one to 32,000,000 centipoises.

*Nine multi-speed (ratio 200 to 1) models as well as four-speed (ratio 10 to 1) and single-speed models are available in various R.P.M.'s up to 100. Each Brookfield Viscometer is accompanied by a complete set of suitable spindles, a convenient spindle holder, and a compact carrying case that holds both the Viscometer and the spindles.

UL ADAPTER

When attached to LV models of the Brookfield Viscometer, the Brookfield UL Adapter, consisting essentially of a cylindrical spindle mounted symmetrically within a concentric tube, provides amplifying effects which make possible measurements to within .2 millipoises in the ultra-low viscosity range of .2 to 10 centipoises.



HELIPATH STAND

When used in conjunction with a suitable Brookfield Viscometer fitted with a special bar-type spindle, the Brookfield Helipath Stand lowers the rotating spindle through the test material, making possible the testing and study of highly plastic materials such as grease, putty, shaving cream, gelatin, shortening, etc.

LEVELING STAND

Designed to provide firm, easily-leveled support for a Brookfield Viscometer when used either by itself or equipped with a UL Adapter, the three-point screw-leveled base and adjustable elevation clamp of the Brookfield Leveling Stand insure fast set-ups and trouble-free determinations.

BROOKFIELD VISCOTROL

Makes Possible Continuous and Automatic Viscosity Control

Based on the same simple yet highly accurate operating principles employed in the portable Brookfield Synchro-Lectric Viscometer, the Brookfield Viscotrol is designed for use where viscosity variations during production normally occur only in one direction. When installed in such tank, vat or pipe production systems, the Brookfield Viscotrol continuously measures the viscosity of the material in process. If a variation occurs, the unit automatically activates danger signals and/or other viscosity controlling devices. *Write today for Data Sheet 012.*

Save Time, Labor, Dollars!

WITH BROOKFIELD INSTRUMENTS

Precision manufacturing and sturdy design, combined with ingenious application of the old and simple principle of measuring with a calibrated spring the torque on a spindle rotating at a constant speed, have resulted in Brookfield instruments becoming the standard the world over for the accurate, fast and direct determination of viscosity and related properties. *Use the convenient coupon below.*

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Brookfield Engineering Laboratories, Inc. **B**
Stoughton, Massachusetts

Gentlemen:

Please send me the literature items I have checked below:

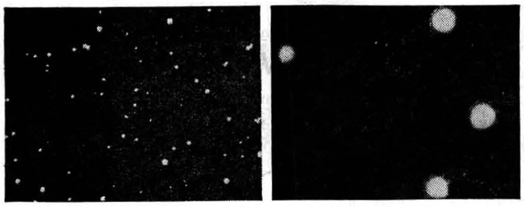
☐ Fully illustrated catalog showing all portable Brookfield Viscometers and accessories.

☐ Brookfield Viscotrol Data Sheet 012.

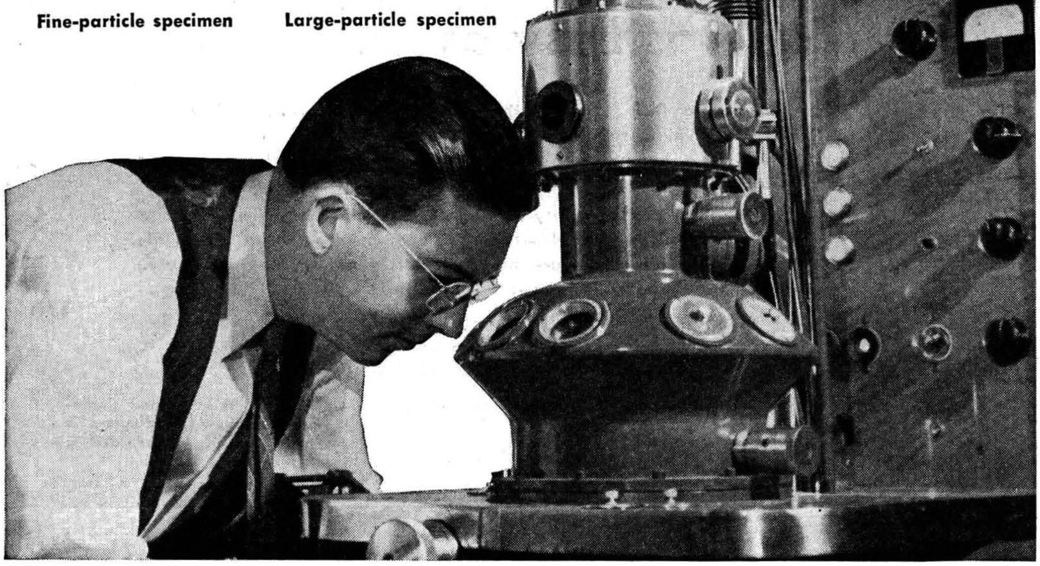
Name:______________________________

Address:____________________________

Synthetic latex, magnified 7500 x



Fine-particle specimen Large-particle specimen



Dr. C. F. Eckert, operating the RCA Electron Microscope in the General Laboratories of the U. S. Rubber Co. Resolution and magnifying power is 20 to 50 times greater than the best light microscope—with 75 to 100 times greater depth of field

How the RCA *electron microscope* helps U.S. RUBBER "tailor-make" synthetic latex to order

Says the U.S. Rubber Company:

"We undertook the study of synthetic latex to see if particle size had some relation to problems connected with dipping products—like balloons and rubber gloves, for instance. Latex would not dry readily. Nor could it be concentrated easily.

"With the aid of the RCA Electron Microscope, we found that synthetic rubber latex could be improved for dipping—if we made it up in larger particles. Also, with the instrument we were able to study the effects of many ingredients on particle size.

"Result: Today we can regulate the particle size of synthetic latex, not only to improve it for dipping, but also to make small-particle latex that readily penetrates between cloth and paper fibers—for better impregnation."

This is another example of how RCA Electron Microscopes are helping industry solve fundamental problems of product research and processing. For information on the usefulness of the RCA Electron Microscope in your field, write Department 11 B, RCA Engineering Products, Camden, New Jersey.

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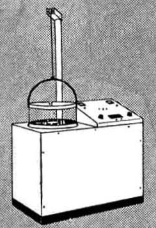
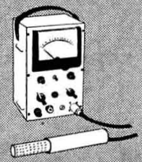
Micro-second Timer



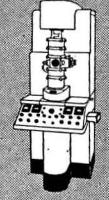
Vacuum System

Vacuum Gage

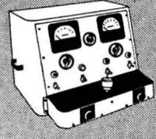


Count-Rate Meter

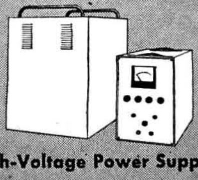
New Low-Cost Electron Microscope



Electron Diffraction Unit



Vacuum Leak Detector



High-Voltage Power Supplies

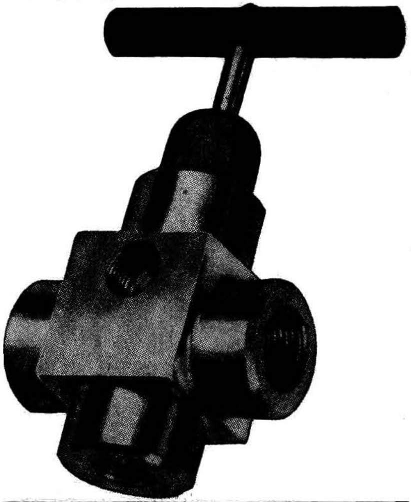
the analyst's column

PRECISE and unambiguous writing is the hope of every scientific author, and the despair of most editors. The fact that words change meaning through careless usage or are extended to express more than originally intended adds to our difficulties. The occupant of this corner has of necessity some experience with the problems of scientific nomenclature, and can appreciate the concern and impatience of those who wish to do something about it. We are continually adding, of course, to our knowledge, and so language must change to express our thoughts adequately. It is a clumsy medium at best, because rather than coin a new word we are prone to give added meanings to older ones. Those who are continually coining new words hold that they have the best solution to this age-old problem, and those who point out how illogical some definitions are, often convince us of their logic but not always of the best way of correcting the definition.

There are many critical readers who are annoyed by multiple shades of meaning given to certain well-known and supposedly well-defined words. Most of us mutter to ourselves and do nothing. But Wm. Rieman III, professor of analytical chemistry at Rutgers University, is disturbed about a word commonly used but beginning to cover too much ground because of improper usage, and he has been thoughtful enough to write us about it.

> I suggest that you put a plea in "The Analyst's Column" for uniformity in the use of the word "occlusion" as it pertains to coprecipitation. The use of this word in an unusual meaning in a recent article set me off on a search through all the important textbooks of quantitative analysis to see how the various authors treat this word.
>
> Eight of the books use occlusion to denote the phenomenon in which foreign ions are adsorbed by the growing crystals of the precipitate and subsequently trapped or buried beneath the

(*Continued on page 17A*)



THE ANALYST'S COLUMN

surface by the continued growth of the precipitate. This is the sense in which Kolthoff used the word in his excellent article on the "Theory of Coprecipitation" [*J. Phys. Chem.*, **36**, 860 (1932)]. It should be unanimously accepted as the definition of occlusion.

Two books use occlusion to mean the mechanical entrapping of some of the mother liquor by the crystals of the precipitate. Since the weight of the trapped mother liquor seldom exceeds a few tenths of a per cent of the weight of the precipitate and since most analytical precipitates are obtained from dilute solutions, it follows that only insignificant amounts of foreign salts are ordinarily coprecipitated by this mechanism. Furthermore, the highly specific nature of coprecipitation is another proof of the minor role played by the entrapment of the mother liquor. If such entrapment were responsible for coprecipitation, all constituents of the solution would, of course, be coprecipitated in proportion to their concentrations. If this minor phenomenon is to have a name, let it be entrapment or inclusion, but not occlusion.

One of the books examined uses occlusion as synonymous with coprecipitation. There is no need for such a synonym.

WE were interested in glancing through an iron and steel program held in Spain, to pick out the papers dealing with analyses. Sorry abstracts were not available, but at least the topics may interest you. The occasion was the Second General Assembly of the Institute of Iron and Steel, Madrid, Spain, December 10 to 15, 1951.

Application of Physicochemical Methods of Metallography to the Mineralogical Analysis of Iron Minerals. ALBERT PORTEVIN.

Methods of Chemical Analysis. CASIMIRO GONZALEZ.

Gravimetric Determination of Molybdenum in Steels with Oxiquinoline. JOSE NAVARRO ALVARGONZALES.

Determination of an Adiabatic Modulus of Elasticity. JOSE PEREZ REYNA.

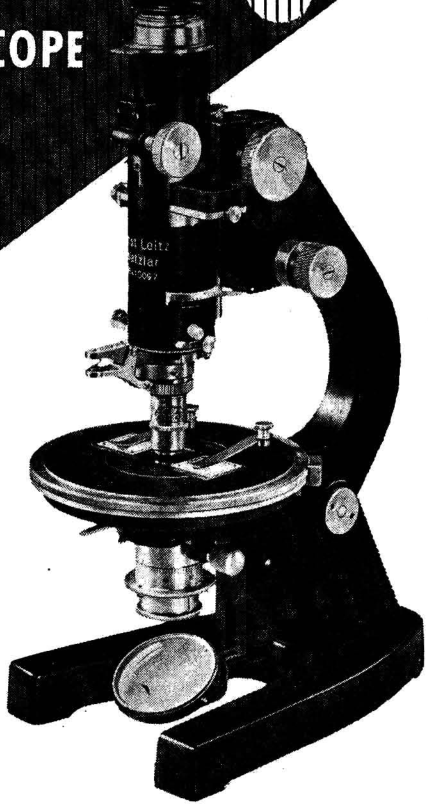
Statistical Methods in the Steel Industry. PEDRO MENDIZABAL.

Spectrographic Measurement of the Diffusion Constant of Carbon in a Cemented Steel. ANTONIO CAMUÑAS PUIG AND ENRIQUE ASENSI ALVAREZ ARENAS.

Some Statistical Considerations on the Chemical Analysis of Fusions. M. GUELAIN.

L. T. Hallett

Associate Editor



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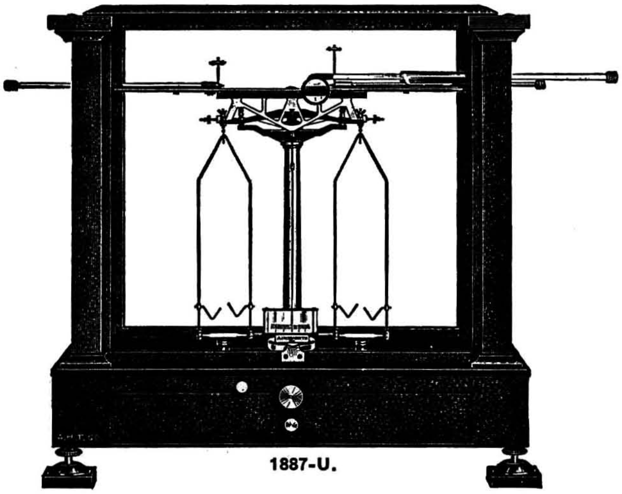

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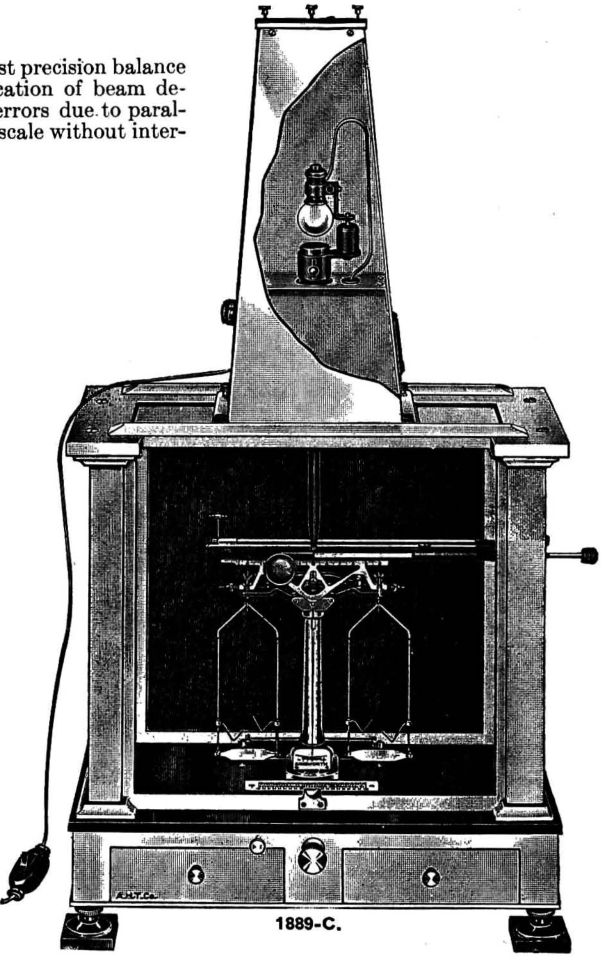

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ANALYTICAL CHEMISTRY

Walter J. Murphy, Editor

Melvin G. Mellon—1952 Fisher Award Winner

For outstanding contributions to the science of analytical chemistry, Melvin Guy Mellon has been selected to receive the 1952 Fisher Award. We believe that this was a wise selection—that Dr. Mellon richly deserves this high honor.

We feel particularly proud to have had Dr. Mellon on the Advisory Board of Analytical Chemistry during eight critical years of the publication's history. He was a member of the original board which your editor activated when he was appointed to his present post in 1943. Dr. Mellon served until 1951, when he was automatically retired under the rotation plan adopted in 1949. We note in our records that he attended every board meeting, many times at great personal sacrifice.

Dr. Mellon took an active part in early discussions of just what should be the role of Analytical Chemistry. Many hours were spent in working out the problems incident to setting up Analytical Chemistry as a publication separate from *Industrial and Engineering Chemistry*. On this and many other occasions, his advice and counsel were invaluable. Although a recognized specialist, Mellon retained the broad view and exhibited the knowledge of the entire field necessary for the important decisions on fundamental policy.

He has developed an enviable reputation as a teacher, author, and speaker. During more than 30 years of association with Purdue University, his contributions to the teaching of analytical chemistry have been great. One of his unusual endeavors was the filming of a 16-mm. movie as a visual aid in teaching laboratory technique. An academic colleague has described him as "an untiring investigator and a leader, who, through his influence upon his graduate students, has inspired others to scientific achievements in analytical chemistry."

Dr. Mellon's principal undergraduate teaching assignment at Purdue has been the course in elementary quantitative chemical analysis. In 1937 he published "Methods of Quantitative Chemical Analysis," in which he presented the material from the functional viewpoint of unit operations of separations and measurement applied in multicomponent analyses. A new edition with P. J. Elving as coauthor is soon to be published.

Dr. Mellon has directed research which has brought colorimetry to its present stage of development. In 1933 he secured for his laboratory the first instrument produced on the model of the General Electric photoelectric spectrophotometer designed by Hardy at MIT. The latest model of the Hardy instrument, as well as the original production instrument, is operating in his laboratory. His pioneering work with the spectrophotometer is generally recognized. He served as editor of "Analytical Absorption Spectroscopy," the comprehensive text and reference book, prepared in collaboration with eight other specialists, published in 1950. Dr. Mellon deserves much credit for seeing the need for placing colorimetric analysis on a quantitative physical measurement basis.

Purdue University recognized his sound thinking and good judgment early in his career, and in 1928 appointed him chairman of the Chemistry Building Planning Committee. He visited many academic, industrial, and governmental laboratories in connection with this planning. As construction on the final wing moves to completion, Dr. Mellon can look with pride on a job well done.

In addition to important papers on colorimetry and spectroscopy, Mellon has frequently contributed valuable papers in other fields of analytical chemistry. He has been especially interested in the use of the library, preparation of bibliographies, and systematizing chemical nomenclature. As an outgrowth of his course at Purdue, he prepared "Chemical Publications," which has been widely adopted as a standard text. More recently he initiated a course designated as Chemical Writing, believed to be the only course of its kind being taught in a chemistry department.

Dr. Mellon has always given freely of his time as a committee member or a speaker. He is a member of the important Committee E-3 (Chemical Analysis of Metals) of the A.S.T.M. organized by the late G. E. F. Lundell. He was first chairman of the Committee on Naming Methods in the ACS Division of Analytical Chemistry. He has addressed more than 50 local sections of the ACS, usually speaking on colorimetry, spectroscopy, or chemical literature.

As he joins the illustrious group of Fisher Award winners—Furman, Lundell, Kolthoff, and Willard—we extend our hearty congratulations to Melvin G. Mellon. Each and every member of the editorial staff has felt free to ask his advice and assistance frequently. Analysts everywhere join in this heartfelt tribute to a great leader in the field of analytical chemistry.

4th Annual

Review of Analytical Chemistry

CONTINUING our review of developments in analytical chemistry, the following nine articles report progress in important fields of application. The fundamental developments were reviewed in the January issue. A combined reprint of reviews from both issues is available at $1.50 per copy from the Reprint Department of the AMERICAN CHEMICAL SOCIETY.

—The Editors

COATINGS

T. G. ROCHOW AND R. W. STAFFORD
American Cyanamid Co., Stamford, Conn.

THE analysis of coatings is the concern of this review. It covers chemical and physical analytical methods applicable to organic high polymers and associated oils, waxes, pigments, and plasticizers, as disclosed in the literature during the past year. The scope of materials includes lacquers, varnishes, and paints, and also organic finishes for or on paper, textiles, leather, and metals. The treatment is abridged by arbitrarily excluding other important materials such as vitreous enamels, metals, and chemically treated metals, and by disregarding what are considered to be the less common uses.

Following the arrangement of last year (*55*), general analytical schemes are considered first. The next section is devoted to the generally applicable resinography and related topics, the fundamental importance of which is evidenced by the increasing activity in this field. Monographs on the analysis of component parts of organic coatings are then considered in the order: separate classes of resins, oils and waxes, pigments and plasticizers, and specific constituents or functional groups. Auxiliary references to a limited bibliography on relevant descriptive or evaluative literature are presented as generally helpful background information.

GENERAL ANALYTICAL SCHEMES FOR ORGANIC COATINGS

A number of investigators have reported on general procedures which are directly or potentially applicable to the identification of high polymeric constituents of organic coatings.

Nechamkin (*48*) classifies thirteen common types of plastics according to their behavior on fusion with metallic sodium. After separation into six groups, distinctions within each group are made by observing the solubility and the characteristics of burning. This simple procedure permits typing an unknown plastic.

For the separation of high polymers by appropriate solvents, Thinius (*66*, *69*) gives directions for the resolution of mixtures of cellulose ethers and esters, chlorinated rubbers, polystyrene, and polyisobutene into their components by selective extraction of the dry solids with various solvents and solvent mixtures. In a subsequent publication (*68*), Thinius reports on the extension of this work to include new data on nitrocellulose, on distinguishing polymers according to their tolerance toward diluents, and on distinguishing various degrees of substitution in saponified vinyl and cellulose esters. Di Noia (*20*), in an attempt to separate mixtures of natural and synthetic resins with organic solvents, tabulates the physical and chemical properties of a number of resins available in Argentina. He includes solubilities in common organic solvents and finds that fifteen such solvents, plus water, are sufficient to separate most polymer mixtures, prior to the application of a recommended systematized analytical attack.

Castle (*12*) suggests dichloroacetic acid as a color reagent for natural and synthetic resins. Colomb (*16*) points out that the Liebermann-Storch-Morawsky test for rosin can be applied to many other paint and varnish materials, including natural and synthetic resins, vegetable oils, and plasticizers.

In a fairly recent PB report (*32*) 17 analytical methods for plastic materials, as used by I. G. Farbenindustrie, are listed. Polyvinyl compounds, plasticizers, urea compounds, and polychloroprene are covered.

In the field of generally applicable analytical methods, Toeldte and Hezel (*70*) critically discuss the determination of the saponification value by Hezel's method (*29*), which was cited in a previous review (*55*). Hahn (*25*) recommends potassium hydroxide dissolved in a 1 to 1 mixture of Cellosolve and xylene as an ideal reagent for the determination of saponification numbers. Shaefer and Balling (*59*) discuss the saponification of difficultly saponifiable esters, as exemplified by rosin esters, using a diethylene glycol-phenetole solution of potassium hydroxide, and titrating the potassium salt formed by the Riemann double indicator method. Lenz (*44*) recommends the use of a 40-60 methanol-benzene mixture in a Soxhlet-type apparatus to extract oil from pigment pastes. Thinius (*67*) suggests tetrahydrofurfuryl alcohol containing potassium hydroxide as a good agent for the determination of chlorine in aliphatic polymers.

Smith and Shaw (*63*) have prepared a bibliography on resin analysis as a contribution from the Subcommittee on Resin Analysis of the Plastics Committee of the Technical Association of Pulp and Paper Industries.

RESINOGRAPHY AND RELATED TOPICS

At the Annual Meeting of the Electron Microscope Society of America at Franklin Institute in Philadelphia, November 8, 9, and 10, 1951, several announcements were made which are of interest in the coatings field. E. B. Bradford of the Dow Chemical Co. studied electron microscopically the effects of plasticizers on the surface structure of films left by synthetic latices intended for the paint, paper, and textile industries (*14, 35*). He concluded that poor films result from lack of coalescence of the droplets of polymer. "Plasticizers" cause coalescence in various ways, depending on the polymer: with saran, by reducing the surface tension of the droplets; with polystyrene, by serving as a lubricant in facilitating closer packing of the droplets; with polyvinyl plastics, and in this case an internal plasticizer, by the extension of the particulate surface area to wormlike shapes rather than spheres. The uniformity of dispersion of pigment was also pictured in formulated latices.

James Hillier of the Radio Corp. of America, using carefully corrected electron objectives and taking precautions to minimize specimen contamination, focused exactly on particles of carbon black and showed surface reticulations less than 20 A. across (*14, 35*).

Virgil Peck and Wilbur Kaye of the Tennessee-Eastman Corp. etched and replicated the surfaces of cellulose acetate fibers and films (*14, 35*). They found that water in the plastic has a pronounced effect on the nature of the etched surface. They explained that water may be insulating the chain molecules of polymer from one another.

Electron microscopy increasingly facilitates differentiation and recognition among varieties and species of clays, pigments, and other particulate materials of interest in the coatings field. Max Swerdlow *et al.* (*35*), compare the electron microscopic morphology of kaolinite *vs.* halloysite with the data obtained by differential thermal analysis and x-ray diffraction. B. M. Siegel (*35*) studied homoionic montmorillonites. Kerr and a large team of coworkers have reported (*42*) to the American Petroleum Institute on the chemical, thermal, x-ray, light and electron microscopic, and infrared-absorption analyses of "known" samples of most of the commercially valuable species of clay and clay-like materials. This is the most comprehensive description of clays yet assembled.

Ames and Sampson (*1*) publish results of an electron microscopical study of the surfaces of films of nitrocellulose, unplasticized *vs.* plasticized with castor oil or dibutyl phthalate. The film containing castor oil showed a granular surface composed of grains up to 0.1 micron in diameter, whereas the film with dibutyl phthalate was as apparently homogeneous at 20,000 × as the unplasticized film. Thus, the homogeneity, low permeability, and thermoplasticity of the dibutyl phthalate plastic can still be explained by the Doolittle (*20A*) hypothesis that the dibutyl phthalate remains in the film as a nonvolatile solvent, preventing aggregation of the polymer molecules, reducing the formation of micelles, and resisting exudation on heating. The castor oil, however, exudes readily and leaves a permeable film of nitrocellulose. Apparently, the castor oil acts as a mechanical plasticizer— i.e., it separates the relatively small aggregates of polymer molecules.

Richards (*52*) shows that, by polymerizing ethylene under various conditions of temperature and pressure, a wide range of polymers is obtained, including oils, greases, soft and hard waxes, and plastics both softer and harder than the familiar type of polymer used for electrical insulation and film. Some of these variations in properties are due to changes in molecular weights and their distribution; others are due to degree of chain branching (with commensurate degree of crystallinity). Some electron micrographic data are given, but the writers understand from conversation with Richards that more electron microscopical information on polyethylene is forthcoming.

Rochow, Botty, and Rowe (*53*) studied the drying of linseed oil electron microscopically. They found that a film of low-viscosity, varnish-grade linseed oil, containing butyl catechol as inhibitor, contains particles around 20 A. in diameter, corresponding to a macromolecular weight of 2500 or less. Without inhibitor, the particle size of the oil film increases noticeably within 20 minutes of air-drying and within 1 week of drying, the particle size reaches a magnitude of about 80 A. in diameter or about 160,000 in molecular weight. By the addition of drier or by heat-bodying the oil before casting a film, intermediate particle sizes are obtained. In all the dried films, the particles show a tendency toward zigzag alignment and felting of such strings. This may suggest the mechanism of film formation. Polyacrylonitrile in thin films shows a tendency of its fundamental particles to form stringers, and more strongly, to aggregate in rounded groups.

Synthetic foils—i.e., self-supporting films—are being studied microscopically. Vieweg and Moll (*72*) used light microscopy, particularly with the aid of phase contrast, to show the surface structures and to show the distribution of dyes and fillers, especially in plasticized polyvinyl chloride. Some insight into the internal structure of the polymer is gained by the use of polarized light to observe the effect of a solvent on the double refraction of the foil. A hot stage permits the variation of temperature during such experiments.

SPECIFIC CLASSES OF HIGH POLYMERIC MATERIALS

A considerable amount of interest has been shown in the problem presented by the analysis of styrenated alkyd resins and oils. Kappelmeier and his associates (*37–39*) report that data collected by chemical methods, particularly saponification values, on four Dutch commercial styrenated oils indicate that a large proportion of the fatty acids is linked to styrene and distributed over fractions possessing different properties. Separation of the various fractions by selective solvents indicates that the styrenate oils in question contain little, if any, neutral polystyrene. The location and nature of the apparent linkage of styrene and/or polystyrene to the fatty acids still remain an open question. Bokhout (*5*) describes a new analytical method for styrenated oils and alkyd resins, based on differential saponification with alcoholic potassium hydroxide, and further states (*7*) that if a styrenated linseed oil is saponified with alcoholic potassium hydroxide in the presence of xylene, an aqueous solution of the dried reaction product yields a white precipitate on treatment with methanol. The precipitate is insoluble in water and is considered to be polystyrene. Bokhout's conclusions have been criticized by Kappelmeier and van der Neut (*36*) and the criticism has been answered by Bokhout (*6*). Petit and Fournier (*50*) claim that the mass polymerization of styrene, α-methylstyrene, benzoyl peroxide, and linseed (or tung) oil at 160° to 300° C. yielded no copolymers, but only a mixture of polystyrene and oil. The oil reportedly contains a small proportion of an addition compound of one fatty acid chain with one styrene molecule. Baltes (*2*) reviews the chemical analysis of "styrolized" oils.

Bischoff (*4*) describes a method for the identification of modified and unmodified phenol-formaldehyde resins which is based on the liberation of the phenol by fusion of the resin with potassium hydroxide followed by testing of the solution with *p*-nitroaniline diazonium salt. Chatfield (*13*) discusses *tert*-butyl, octyl, and phenyl phenol varnish resins and briefly reviews fourteen tests to be conducted.

Mann (*46*) presents a detailed discussion of the application of infrared spectroscopy to the qualitative and quantitative estimation of polymers used in the rubber industry. Goldspiel and Bernstein (*24*) describe the application of x-ray diffraction methods to the identification of natural and synthetic rubbers. Cianetti (*15*) detects chlorinated rubber in varnishes by the hydrogen chloride evolved from the pyrolyzed film and adds directions for quantitative separation.

Haslam and Clasper (*27*) list methods for the analysis of mixtures of hexamethylenediamine and amino caproic acid isolated as the hydrochlorides in the acid hydrolysis of nylon-type polymers. The latter is determined by titration to a phenolphthalein end point with standard sodium hydroxide solution. To estimate the former, the mixture of chlorides is passed through a column of Amberlite IRA-400 and the hexamethylenediamine compound is titrated to a methyl orange end point with sodium hydroxide solution. Zahn and Wolf (*74*) describe the analysis of polyamides and polyurethanes, giving details of the paper chromatography of the amino and dicarboxylic acid components.

In discussing the analysis of silicon organic compounds, Kreshkov and Bork (*43*) describe a chemical test for the detection of silanes in technical products and list a series of color reactions to differentiate among alkyl and aryl chlorosilanes, alkyl and aryl alkoxysilanes, tetraalkyl silanes, and others. Rochow and Rochow (*54; 138*, pp. 120–30) give some properties and molecular weights of some silicone polymers.

Conner and Eyler (*17*) give details of a method for the analysis of sodium carboxymethylcellulose. Schrenk (*58*), in discussing methods of test for nitrocellulose, includes methods for its detection and estimation in mixtures, as well as the determination of nitrogen content.

Swann (*65*) has developed a colorimetric method for the determination of rosin and rosin esters in paints and varnishes, which is a modification and extension of the Liebermann-Storch acetic anhydride–sulfuric acid test, and which employs an electrophotometer. DeBaun and Nord (*18*) carry out the phloroglucinol-lignin color reaction in a spectrophotometer cell and measure the optical density as a function of time. Data are given for lignins from a number of hard and soft woods.

OILS AND WAXES

Kawakami and Miyayoshi (*41*) present a discussion of the ultraviolet absorption spectra of a wide variety of fatty oils, and of the relationship between absorption spectrum, composition, and drying properties. Newey and his colleagues (*49*) report on the segregation of fatty acids and their derivatives by extractive crystallization with urea. When allowed to react with urea, the more saturated components form insoluble adducts. Numerical data on the segregation of various fatty acids and derivatives are given. Kaufmann and associates (*40*) describe a spectroanalytical method for the determination of conjugated diene, triene, and tetraene fatty acids. Artificial mixtures of various proportions of 9,11-linoleic, eleostearic, and parinaric acids are analyzed as illustrative examples. Shreve and associates (*62*) have determined the infrared absorption spectra of nineteen pure long-chain saturated and mono-unsaturated fatty acids, methyl esters, triglycerides, and alcohols. The absorption bands are correlated with molecular structure. These investigators (*61*) have also used infrared spectrophotometry to determine the *trans*-octadecanoic acids, esters, and alcohols in mixtures, and prove the accuracy and precision of the method by analyses of nineteen synthetic mixtures of acids, esters, and alcohols of known composition. Cassidy and Nestler (*11*) discuss the principles and methods of application of chromatography as used in the separation of fatty acids. The review covers the application of elution analysis, frontal analysis, displacement analysis, and partition chromatography. Boldingh (*8*) describes the quantitative separation of the saturated C_6-C_{18} fatty acids by paper or column chromatography, using benzene absorbed in vulcanized rubber as the immobile solvent, and a strong polar solvent as the mobile phase. As regards the fatty acids of lower molecular weight, Fairbairn and Harpur (*22*) give details of the chromatographic separation of the saturated C_2-C_8 fatty acids from a single small sample, and Moyle and associates (*47*) describe the separation and estimation of similarly composed samples on buffered partition columns.

Ivanovszky (*33*) presents a discussion of the various chemical and physical analyses of waxes, and their significance. He proposes an analytical scheme comprising preliminary tests, such as ash, elementary analysis, etc.; physicochemical tests, such as acid and ester values, melting-setting points, viscosity, etc.; and technological and scientific examination, such as colloidal phenomena, mechanical properties, oil absorption, performance tests, etc. Sadtler (*56*) reports on the infrared absorption spectra of eighteen waxes.

PIGMENTS AND PLASTICIZERS

Carman and Malherbe (*10*), in measuring the surface of paint pigments and other fine powders, compare the gas permeability method with those data obtained by one or several of the following: nitrogen absorption, liquid permeability, methyl stearate absorption, light and electron microscope, and sedimentation. Hunt, Wisherd, and Bonham (*31*) present the infrared spectra of 54 powdered minerals and pure inorganic compounds, and make a tabulation of the principal absorption bands. Included among the minerals are many of interest to the paint industry.

Haslam, Soppet, and Willis (*28*) have prepared a thorough treatment of the problem of analyzing plasticizers obtained from polyvinyl chloride compositions. A method of separation is described and a series of general and specific tests is listed. Directions for the separation of alcoholic components of ester-type plasticizers, and of cresols from phosphate plasticizers are given, and include a semimicro method and apparatus for the former. Identification is accomplished by a correlation of chemical and infrared spectroscopical methods. In a second section devoted to infrared spectroscopy, individual plasticizers are identified by comparison of their spectra with those of known standards. Reproductions of nineteen such are included, together with descriptions of the most characteristic bands for phthalates, phosphates, and long-chain aliphatics. Mixtures are discussed in considerable detail. Use is made of the spectra of the separated acids and alcohols to resolve difficult cases. Semiquantitative results are obtained by comparison with the spectra of mixtures of known composition. This procedure is also applied to estimating relative proportions of mixed alcohols, as illustrated by a composite spectrum.

SPECIFIC CONSTITUENTS

This section includes separate constituents of coating materials. Haslam and Clasper (*26*) separate mixtures of adipic and sebacic acids by adding sufficient sodium hydroxide solution to neutralize the adipic acid alone, and then extracting with ether in a continuous extractor. Shreve and Heether (*60*) propose an ultraviolet spectrophotometric method for the determination of total phthalic anhydride in alkyd resins and other phthalate esters. After isolation of the phthalic acid as dipotassium phthalate monoalcoholate, by the usual saponification procedure, the salt is washed with water into a volumetric flask and the solution is acidified and made up to volume. Comparison of the ultraviolet absorption spectrum of this solution with that of a standard permits the quantitative estimation of the per cent phthalic anhydride in the original ester. The method is currently being studied cooperatively by Subcommittee XI of Committee D-1, American Society for Testing Materials. Vaskevich (*71*) converts phthalates to the dipotassium salt with potassium hydroxide. Treatment with sulfuric acid converts the salt to the anhydride, which is then fused with resorcinol to yield fluorescein. Sandermann (*57*) suggests a new color test for rosin acids, which, when combined with the Liebermann-Storch test and the determination of the maleic anhydride value, permits the rapid identification of commercial rosin products. Brown (*9*) describes the separation of fatty acids containing more than one carboxyl group by paper chromatography. Stark, Goodban, and Owens (*64*) give directions for the chromatographic separation of a number of dicarboxylic acids on ascending columns.

Wurzschmitt (*73*) used two new methods to analyze mixtures of monoethylene glycol, diethylene glycol, and diethylene glycol monoethyl ether: (*1*) Monoethylene glycol alone reacts with alkaline copper sulfate to give a blue complex; the intensity of the color is used to estimate the quantity of the glycol, and the others are determined indirectly from the density; (*2*) diethylene glycol monoethyl ether is insoluble in 72.5% potassium hydroxide solution. Jaffe and Pinchas (*34*) estimate dipentaerythritol in the presence of pentaerythritol by the infrared spectroscopy of the corresponding acetates in carbon tetrachloride. MacBeth and Thompson (*45*) present data for determining the composition of aqueous propylene glycol solutions by measuring the density at 35° C. and the refractive index at 25° C. Pohle and associates (*51*) submit the report of the Glycerol Analysis Committee. Collaborative work shows that the sodium periodate method is more reproducible than the periodic acid method. The former is presented in detail.

Bennett (*3*), in reporting on qualitative tests for formaldehyde, reveals that collaborative study indicates that the Hehner-Fulton and the chromotropic acid methods are satisfactory. Details of the procedures are given. Duong (*21*) proposes the reaction with *m*-phenylenediamine, followed by the addition of hydrochloric acid and oxidation with ferricyanide, as a new method for determining formaldehyde.

Friedel (*23*) records the infrared spectra of 22 phenols examined in carbon disulfide solution. Densham and Armstrong (*19*) describe the cell and the analytical procedure used in the analysis of alkyl phenols by infrared spectroscopy. Hossfeld (*30*) couples simple phenols with diazotized sulfanilic acid and chromatographically develops the sodium salts on carbonate-treated paper with ethyl acetate–water. Results are given for a number of phenols.

ACKNOWLEDGMENT

The authors wish to acknowledge with appreciation the assistance of their colleague, James F. Shay, in keeping current the literature file on which this review is based.

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FOOD

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THE present review covers the period of about December 1950 to November 1951. It is a sequel to the review of methods of food analysis for the period December 1949 to November 1950 (*124*).

MOISTURE

Improved methods of determining moisture in a variety of food products are still sought. Several papers in this field appeared in a symposium for moisture determination (*58, 127, 182, 186*) and one paper from France has made a critical review of numerous methods, giving particular attention to the procedure of Karl Fischer (*20*).

Earlier work by Shaw *et al.* (*159*), reported in a previous review (*124*), showed that magnetic absorption by protons may be used to measure water content in the range encountered in natural and dehydrated biological materials, energy absorption varying linearly with the amount of water in the tissue. A more recent paper by these workers (*160*) discusses new measurements of proton magnetic resonance for a number of hygroscopic substances containing up to about 20% water.

A new approach to the determination of water in fruits and vegetables has been proposed (*107*), the organic content of the sample being measured by the quantity of potassium dichromate required to oxidize it. Water content is then determined by difference.

Replacement of dry methanol in the Karl Fischer reagent by formamide has been suggested in the determination of moisture in dehydrated vegetables (*114*). A discussion of relative merits of the Karl Fischer method and other methods of estimating water in molasses will be of interest to sugar chemists (*46*).

A rapid method of determining water in fruit purees and concentrates involves employing a suitable desiccant to absorb the water from the sample (*143*). The increase in weight of the absorbent, corrected by a blank, represents the moisture content of the sample. Rapid methods have also been suggested for moisture determinations in sausage products (*65*) and in grains (*9*), the latter being based on the determination of the dielectric constant of the whole grain, which can be obtained in a few seconds and translated to moisture content with an accuracy of ±0.2%.

Package designers for protection of food during storage will be interested in the graphical interpolation method for measuring equilibrium relative humidity (*103*). The basis of the method is that a material does not change in weight when exposed to an atmosphere of equilibrium relative humidity. This condition is determined by graphical interpolation from data on rate of change of weight at different humidities. The method is applicable to a wide variety of foods and is simple, inexpensive, and rapid. In this connection, a recently published method for measuring the rate of transmission of organic vapor through various packaging materials should also be of interest to package designers (*130*).

Because all analytical moisture methods involve manual manipulations, considerable time, and certain degrees of technical skill, efforts are continually being made to devise an instrument that will measure moistures rapidly, easily, and accurately. It has been reported (*67*) that the Brown-Duvel and Steinlite instruments are adaptable for determination of moisture in sweet corn for canning. The Sicco-Rapid moisture tester and the large Turbosicc unit used by German maltsters for grain when compared with oven methods were found to give comparable results with considerable savings in time (*59*), and it has been reported that the Brabender tester could be used for total solids in milk (*192*). From England comes a report of another instrument for measuring moisture in grains, based on electrical conductance (*24*). The instrument is portable for field use. A new apparatus for determining moisture in oils and dried foods appears to constitute an improvement in the old toluene or xylene distillation method (*61*). Accuracy is said to be of the same order as results obtained by the Karl Fischer technique. A so-called "moisture balance," said to be especially designed and built for rapid and accurate determination of moisture in a wide variety of materials has been described (*37*). The balance incorporates both weighing and drying components, utilizing infrared radiation for drying and a null-point torsion balance for weighing.

PROTEINS AND AMINO ACIDS

Modified macro, micro, and semimicro-Kjeldahl apparatus have been described (*86*, *161*, *163*) for greater speed and accuracy.

Techniques and reagents for chromatography of amino acids have been suggested in recent articles (*29*, *64*, *178*), and the importance of controlling the water content of solvents used in paper chromatography of amino acids has been pointed out (*162*, *168*). Increased water content of the solvent generally increased the R_f value of 23 amino acids investigated. Small scale filter paper chromatography has been fully discussed in a recent publication (*151*), and a review of paper chromatography of amino acids as applied to plant products and food chemistry from 1949–1951 comes from France (*14*).

It is said that chromatograms of amino acids run with phenol will be destroyed if dried above 27° C. (*28*). Drying at 60° to 105° C. for 5 minutes leads to marked destruction and with casein hydrolyzate all α-amino acids were partly destroyed during evaporation of phenol, but to different degrees. It has been found (*31*), however, that good definition with only moderate attack on the paper can be obtained by using butanol solutions of phenol (0.2%) with an equal volume of 0.25 N hydrochloric acid in butanol. By employing several solvents buffered at pH values between 1.0 and 12.0, it is possible to separate each amino acid from all the others by use of one-dimensional chromatography (*115*). Mesityl oxide has been suggested as a solvent (*30*), spread of values being considerably higher than with collidine, and almost as high as with phenol. In addition, it has great rapidity of migration. Mesityl oxide does, however, have a tendency to oxidize and polymerize on standing.

The effect of pH on various amino acids was demonstrated by the use of 83 graphs (*104*). Quantitative microdetermination of amino acids has been achieved by localizing the spots on the paper chromatograms and lightly marking their limits by pencil under ultraviolet light (*137*). The spots are cut out, color is developed with ninhydrin, and color intensity is measured at the end of the reaction.

A relationship has been established between the R_f values on paper chromatograms of peptides and the amino acids of which they are composed (*135*). Thus, from the R_f values of amino acids and two general, experimentally determined constants, the R_f value of any desired peptide can be calculated.

Protein error of indicators first described by Sørensen has been suggested as a method to detect minimum quantities of proteins in paper chromatography (*134*). Bromothymol blue and tetrabromophenolphthalein were used with good results, and buffer and salt solutions were utilized as developers.

A colorimetric method for the determination of methionine (*153*) based on a previously published method (*41*) with certain modifications has been suggested. A spectrophotometric method for microdetermination of methionine is based on the reversible reaction of the amino acid with iodine (*7*). Two or more determinations can be completed in 2 to 3 hours with an accuracy of ± 1%. The method does not differentiate between the D and L forms.

A colorimetric procedure for arginine (*155*), based on improving the method of preparing the hypobromite solution previously reported (*156*), has been described, and other reports deal with the determination of glutamine and asparagine (*32*), and chromatographic determination of the proteins ribonuclease and lysozyme (*83*), these proteins being chromatographed on a resin.

From Sweden comes a paper on the use of tricalcium phosphate as an absorbent in the chromatography of proteins (*176*). Of considerable interest is the chromatography of amino acids on sulfonated polystyrene resins (*128*). Mixtures of amino acids are fractionated chromatographically by elution. The resin columns possess higher resolving power than starch columns and are more convenient to operate.

METALLIC IONS

Improved methods for the determination of copper and iron in dairy products (*138*) and in oils (*125*) have been described. In the former method a combined filtration procedure enables both metals to be determined on the same sample. The carbamate reagent is used for copper and the thiocyanate method for iron. Drop analysis techniques for determining zinc, copper, lead, tin, antimony, and barium in food products have been suggested (101). A micromethod for arsenic has also been reported (96).

A colorimetric test (*36*) for calcium in plant materials, covering a calcium range of 100 to 1000 micrograms involves the precipitation of calcium as oxalate which is removed by centrifuging and then dissolved in a known amount of ceric sulfate, the excess of which is determined colorimetrically.

The use of potassium bromate in high-protein flours for bread baking to increase loaf volume makes methods for rapid determination of this salt in flour and bread of interest. A recent technique which will detect as little as 2 p.p.m. of bromate has been described (*84*). However, other oxidizing substances, such as potassium iodate and potassium persulfate, will interfere. Chlorine and chlorine oxides will not interfere.

FATS

In the oxidative deterioration of fats, aldehydes follow as secondary reaction products of the hydroperoxides initially formed. Aldehydes thus formed contribute significantly to the off-odors and flavors of rancid fatty foods. It is, therefore, of importance to have an accurate method of determining aldehydes, and a newly devised technique is based on the formation of 2,4-dinitrophenylhydrazones of monocarbonyl compounds in benzene solution of the rancid food (*142*). Excess of hydrazene reagent and the hydrazones of the dicarbonyl compounds are removed with alumina and the remaining hydrazones of the monocarbonyl compounds in alkaline solution are determined colorimetrically.

Improved methods for determining peroxide values of fats have also been suggested (*50*, *69*). Of interest is the fact that if the test is carried out at a specified temperature there is a correlation between peroxide values at this temperature and those obtained by active oxygen at 36.5° C. (*69*).

Peroxide values and the Kreis test cannot always be correlated with true rancidity as detected by sensory means. Thiobarbituric acid as a test reagent in determining rancidity, particularly in milk fat, has given encouraging results (*52*, *136*). This test is based on the fact that malonic dialdehyde will yield a red color when heated with 2-thiobarbituric acid reagent. Spectral analysis has revealed the color to be identical with that obtained similarly from oxidized milk fat and closely resembles colors secured in like manner from a number of oxidized lipide materials. Infrared absorption studies of the steam volatile components of autoxidizing milk fat have indicated, too, that this method can detect changes before they are apparent by chemical or sensory means (*80*).

Iodine numbers of oils involve chemical methods and a certain degree of skill. A simple, relatively inexpensive refractometer has been developed which eliminates all chemical procedures (*85*). The refractometer reads directly in iodine number units and the temperature correction thermometer is likewise calculated to read directly in iodine number units. An experienced person can make about 12 determinations an hour. Thus far, the method has been applied to flaxseed and soybean oil. The Hanus method for iodine number has been adapted to paper chromatography (*92*). The reagent used was $I^{139}Br$ in methanol. The sample in heptane is deposited on the paper, the solvent allowed to evaporate, and the reagent added until there is no further fading of color. Radiation is finally measured on the washed paper.

The use of polyoxyethylene as an emulsifier in certain foods makes its determination of importance. A recent method (*113*) depends upon the formation of a complex between polyoxyethylene and the amylose fraction of potato starch. The method is sufficiently sensitive to permit analyses of solutions of polyoxyethylene as dilute as 0.05%.

Mixtures of antioxidants are now widely used in stabilization of lard and shortening. Procedures have been developed for the extraction and colorimetric determination of propyl gallate, butylated hydroxyanisole, nordihydroguaiaretic acid, and tocopherols in lard and shortening (*118*).

Improved methods have been proposed for estimating the fat content of milk (*3*, *27*, *57*), cream (*105*), butter and cheese (*27*, *75*), and chocolate (*188*).

Over 304,000,000 pounds of potato chips are produced annually in the United States, requiring more than 130,000,000 pounds of fat. Rapid control methods are desirable for determining oil in the finished chips. A method giving results within ± 0.5%, and which requires about 25 minutes to complete, has been proposed (*184*). An improved method for determining fat in a number of dairy products and cocoa has been suggested (*171*).

A micromethod for the determination of glycerol has been evolved which depends upon hydrolyzing a fat with 50% potassium hydroxide and converting the freed glycerol to isopropyl iodide with hydrogen iodide in the presence of propionic acid (*15*). The liberated iodide is subsequently titrated with 0.02 *N* sodium thiosulfate.

Nitrogenous lipide constituents such as ethanolamine, serine, and choline have been estimated in minute amounts (5 to 75 micrograms) by chromatography on filter paper (*108*).

Trichloroethylene is sometimes used as a solvent in the extraction of soybean oil and methods of estimating small amounts of this solvent in the oil are important. A recent method (*55*) employs a distillation procedure to separate trichloroethylene from the oil and a colorimetric procedure based on the Fujiwara reaction to determine trichloroethylene in the distillate.

ENZYMES

Amylases, phosphatases, urease, lipase, tyrosinase, and protoclastic and other enzymes have been determined chromatographically on paper strips by descending technique with ethanol or methanol as solvents (*68*). The enzyme on the dried developed chromatogram is located by placing the strip on a thin layer of 2% agar containing the appropriate substrate, incubating, and flooding the agar with the appropriate indicator. The position in relation to the solvent boundary and starting position, of colored or clear spots against the colored background, is noted. Another method separates mixtures of enzymes on paper chromatograms which are developed at pH 6.5 with ammonium sulfate (*164*). The zones containing the enzymes are colored through specific enzyme reactions.

A new method for assay of papain, a proteolytic enzyme, has been proposed in which coagulated egg albumin is used as a substrate (*102*), and a manometric method for determining small degrees of proteolysis has been proposed (*78*). This method depends on the principle that certain ampholytes in alcoholic solution displace carbon dioxide from bicarbonates.

A test for pectinesterase is proposed as an index of pasteurization of citrus juices (*95*). The test is based on the activity of pectinesterase which hydrolyzes methyl ester groups to give acid groups, thus increasing the acidity. The procedure is simple and can be completed in 4 hours.

CARBOHYDRATES

The application of paper partition chromatography to qualitative and quantitative sugar analysis has been the subject of a short review (*152*), and other papers point out the value of paper chromatography in the estimation of different sugars (*47*, *72*, *88*, *116*, *147*, *185*).

A spectrophotometric method for keto sugars and trioses is a modification of the reaction of sugars and aldehydes with carbazole in sulfuric acid (*49*). Under certain conditions, the method permits the quantitative determination of ketohexoses and ketopentoses, trioses, and glycolic aldehyde in the presence of each other.

A micromethod for lactose in dairy products sensitive to from 1- to 10-mg. quantities is a modification of a procedure for determining glucose in blood (*5*). Lactose in dry milk products manufactured by most commercial processes exists in an amorphous state with alpha and beta forms present in approximately the same equilibrium ratio as in fluid milk. In certain manufacturing processes, however, the ratio of α- to β-lactose is altered by crystallization of part of the lactose as the alpha hydrate. A method has been proposed (*38*) for estimating alpha and beta forms, based on the fact that β-lactose can be determined from its rate of crystallization in a saturated lactose solution seeded with crystalline alpha hydrate. Alpha-lactose can be obtained as the difference between the total lactose and β-lactose. The method does not require special equipment and yields results in satisfactory agreement with those obtained by other methods.

Procedures for the evaluation of starches for specific industrial uses have been presented (*33*). These procedures are based on flow characteristics of slurries of ungelatinized starch. Viscosity changes, for instance, are recorded by the Brabender amylogram and can be used to forecast the use characteristics and finished product quality. Paper chromatography has been proposed for determining glucose and maltose in starch sirups (*154*).

Various polysaccharides, amylodextrins, amylopectin, and amylo-fatty acid complexes form purple complexes with iodine. This has been made use of in the development of a spot test after these compounds have been paper-chromatographed with formamide as a solvent (*133*).

Evaluation of low methoxyl pectins by means of the Luers and Lochmuller pectinometer has been suggested (*79*) and a new method of determining pectin has been reported from Italy (*172*) which involves shaking the pectin solution in a graduated cylinder with a small amount of talc, then adding alcohol, shaking again, and reading the volume. It is claimed that determinations can be made in solutions containing as little as 0.0006 gram of pectin

VITAMINS

It was reported (*34*) that after July 1, 1951, the Morton-Stubbs correction for the spectrophotometric method of assay for vitamin

A would be official in Canada. This method was made official in the United States in November 1950. Three other papers on the spectrophotometric method for vitamin A determination will be of interest to workers in this field (*1, 71, 121*).

The important role played by vitamin B_{12} and allied substances in animal nutrition, and in the control of pernicious anemia in humans, makes it important that a satisfactory method be available for determining this vitamin.

The microbiological assay of B_{12} is still under study (*132*) and a critical examination has been made by British workers of different methods (*40, 42, 56, 106, 146*). A microbiological method that is satisfactory for B_{12b}, as well as B_{12}, employs *Lactobacillus leichmanii* ATCC No. 7830 in a basal medium containing vitamin C (*112*). This organism is highly sensitive to inhibitory effects of certain detergents, and detergents retained on the glassware because of insufficient cleaning and rinsing can be responsible for erratic results in microbiological B_{12} assays (*111*).

A study panel appointed by a joint meeting of the U. S. Pharmacopeia Anti-pernicious Anemia Preparation Board and the Vitamin Advisory Board has formulated a microbiological assay procedure for B_{12}-like activity. A statistical analysis of a collaborative study of this method was reported at the spring (1951) meeting of the AMERICAN CHEMICAL SOCIETY at Cleveland, Ohio (*26*). The assay method now appears in the Third Supplement to the U. S. Pharmacopeia (*141*), becoming official January 1, 1952. In conjunction with this method, a U. S. Pharmacopeia reference standard for vitamin B_{12} is available.

A method has been presented for the determination of riboflavin by filter paper chromatography (*189*), and another paper describes the estimation of choline in the presence of B complex vitamins (*8*). In this method choline is precipitated at controlled pH levels by the reineckate procedure, where other members of the B complex are not precipitated. In the paper chromatography of vitamin B_1, the chromatogram was transformed to thiochrome by treatment with sodium hydroxide and potassium ferricyanide and then detected by ultraviolet irradiation (*11*).

Extraction of L-ascorbic acid by saturated sodium chloride was found preferable to phosphoric acid in that there was less destruction of the vitamin using the former solvent (*123*). A photometric technique for vitamin C has been reported for colored plant extracts (*10*). Two microbiological methods have been reported for ascorbic acid. In one (*167*) *Staphylicoccus albus* (ATCC No. 9491) was used with apparent success. In the other (*120*) *Escherichia coli* was used for dehydroascorbic acid. Reduction of dehydroascorbic acid by this organism does not yield complete recovery of ascorbic acid, as some is converted to diketogulonic acid. This loss can be calculated and the dehydroascorbic acid can be determined. A comparison of the 2,6-dichlorophenolindophenol and 2,4-dinitrophenylhydrazine methods with bioassays by the Crampton odontoblast growth method for vitamin C showed that the results of all the chemical methods, as well as the bioassay, were in good agreement for the foods used in the tests (*82*).

The problem of the chemical determination of vitamin D in natural oils and synthetic irradiation products of ergosterol and 7-dehydrocholesterol has received considerable attention over the past 15 years. Relatively little success has been achieved in attempts to find a substitute for bioassays for determining vitamin D potencies, and a recent series of papers (*70*) dealing with chemical methods for vitamin D in natural and synthetic products represents a notable advance in solving this problem. Another paper in this field describes a colorimetric method for estimating vitamin D based on the color reaction produced by vitamin D with furfural in an ethanol solution in the presence of sulfuric acid (*35*). It is not necessary to separate A and D to determine D. Vitamin D in fish oils was estimated by removing vitamin A with bentonite and sterols by digitonin (*66*). Vitamin D was then determined with antimony trichloride. The method is claimed to be nearly as accurate as the biological method. Two satisfactory methods for the separation and identification of very small quantities of cholesterol, ergosterol, 7-dehydrocholesterol, and vitamins D_2 and D_3 have been described (*117*).

Methods for determining vitamin K (*43, 62*) and pantothenate (*77, 177*) have also been recently reported. A new book on vitamin assay methods (*73*) should prove of interest to those working in this field.

It has been recommended that the new chemical method for the determination of nicotinic acid be made official (*174*). This method is based on using sulfanilic acid or Tobias acid as coupling compounds instead of metol, ammonia, and aniline. Chemical differentiation between nicotinic acid and nicotinamide is based upon treating the sample with a 10% aqueous solution of cyanogen bromide and coupling the reaction products with sulfanilic acid (*175*). Absorbancy of the color given by nicotinic acid is about twice that given by nicotinamide at 430 mμ.

ACIDS

Mixtures of different organic acids have been determined by means of the "chromatopack" (a pack of Whatman No. 1 filter paper strips compressed between two stainless steel plates) (*169*), and paper chromatography has been applied for organic acids in sugar beet processing liquors (*169*). Chromatographic techniques have also been used for volatile acids which are applied to the paper as ammonium salts (*93*). The chromatograms are developed in solvents containing free ammonia, so that the acids are present at all times as the completely ionized salts. Spot location after development is accomplished by spraying with bromophenol blue indicator acidified with dilute citric acid.

Rapid methods for the determination of citric acid (*6*) and lactic acid (*109*) in dairy products and in grape juice and wine (*98*) have been proposed. Methods of separation of several nonvolatile carboxylic acids (*25*) and lower fatty acids (*187*) by chromatographic technique have been described. An improvement in the Kohman method for determining oxalic acid in foods is said to yield results more representative of the amount of acid actually in the food (*2*).

Mature hops contain lupulon and humulon, which are monobasic acids. A modified spectrophotometric method has been proposed (*149*) for the determination of lupulon and humulon.

A modification of the direct titration method of Prater *et al.* (*145*) is suggested for determination of sulfite in dehydrated white potato (*144*). The principal change is use of formaldehyde instead of acetone as the sulfite binding agent in determining nonsulfite reducing substances. The procedure suggested appears to be well adapted for control laboratories and inspection stations.

COLOR AND TASTE

Measurement of color in margarine has been the subject of two recent papers (*16, 17*). One is an indirect method (*16*) using a Hunter reflectometer which was found to give results reproducible to 0.1 Lovibond unit. It is necessary to prepare a graph to convert Lovibond color scale to chromaticity coordinates. In the other method (*17*) three filter photoelectric reflectometers were used. From the results thus obtained, the chromaticity coordinate can be calculated and these coordinates converted to Lovibond units.

When widely different chromaticities are not encountered, it has been found that the *a/b* ratio of the Hunter color-difference meter can serve as an index of color grade of tomato juice (*150*). An Italian paper gives graphs for the determination of the reflectance color of tomato conserves using the Beckman spectrophotometer (*39*).

Certain chromatographic properties of 17 oil-soluble certified colors and methods of separation have been described (*183*), and techniques of separation of synthetic colors using aluminum oxide and Whatman No. 1 filter paper have been suggested (*63*). Some food dyes apparently have the property of inhibiting diastatic enzymes, and in this connection the inhibiting action of 17 food dyes on the diastatic decomposition of potato starch has been presented in tables (*48*). Permanent glass color standards for extracted honey are now commercially available (*19*).

Methods of evaluating organoleptic analyses have provoked considerable research. The basic statistical principles underlying the different tests used in such analyses have been extensively described in order to focus attention on their binomial similarity and to correlate the tests with more complex systems (*110*).

Four papers of interest to those engaged in sensory testing of foods discuss in detail the value of the methods used (*45, 76, 139, 180*).

SPOILAGE AND CONTAMINATION

The recent wide use of 2,4-D weed killer (2,4-dichlorophenoxyacetic acid) has led to need for an accurate method for quantitatively determining this acid in very low concentrations in foodstuffs. A method has been suggested for estimating 2,4-D in milk (*122*), which consists of separating the chemical from other constituents of the milk by extracting the fat, and precipitating the casein and soluble proteins. The separated 2,4-D is determined colorimetrically using chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulfonic acid). Concentrations of as little as 0.1 mg. per pint of milk can be determined.

Two suggested methods have been published on the determination of DDT in foodstuffs (*119, 165*).

Quaternary ammonium compounds are not only detergents having useful bacteriostatic properties, but also in many instances possess undesirable toxic characteristics, even in small amounts. They find application in food plants and especially milk processing plants where hazard of accidental contamination must be avoided. Accurate methods for the estimation of quaternary ammonium compounds in foods are, therefore, important. A rapid method which will determine these compounds in milk has been proposed (*126*). With suitable standards for comparison, the method will determine quantities of quaternary ammonium compounds in the range of 5 to 100 p.p.m.

Water added to milk can be detected by a proposed lactometric and freezing point method (*191*). The method will detect 3% added water at the 99% probability level, and 2% added water at the 95% probability level. A solvent-disk method was found satisfactory for determining sediment content, including scorched particles, of roller process nonfat dry milk (*173*).

Mycobacterium tuberculosis is determined in milk by treating the milk with potassium hydroxide and then with a suitable solvent that will liberate the bacteria so that they float toward the upper surface of the mixture (*51*). The upper creamy layer is examined microscopically for *M. tuberculosis*. A comparative study has been made of six new agar media proposed for bacterial plate counts of milk (*140*). Usefulness of tetrazolium salts for the indirect determination of the number of bacteria in milk has shown promising results in Germany (*157*). A dilute solution of triphenyltetrazolium chloride will color the milk red in from 3 minutes to 3 hours, depending upon bacterial population. The irregular results in the bacteriological analysis of edible gelatin have been investigated (*89*) and methods for improving the reliability of the results have been proposed.

A spectrophotometric method for the quantitative determination of methanol in distilled spirits is said to be more rapid and as accurate as the modified Denigé's method (*13*). A spectrophotometer is not essential to the method, and visual comparisons can be made with standard solutions of methanol.

A colorimetric method for estimating peanut skins in peanut press cake has been suggested (*44*) based upon the intensity of the color developed when the cake is refluxed with 95% ethanol containing 1.25% hydrochloric acid. A calibration curve must be prepared for each variety of peanut used.

A test for the freshness of meat is based on the intensity of a color reaction obtained from the phosphine, which it is claimed is released from the meat (*166*).

MISCELLANEOUS

British standard methods for the chemical analysis of fluid milk (*21*), of condensed milk (*22*), and of dried milk (*23*) have been released. Two recent books on food analysis (*87, 91*) should be of interest to analysts engaged in this field. Progress in chromatography from 1938 to 1947 has been reviewed (*193*). A recent book on statistical methods (*190*) should also be of interest to food analysts.

Methods of preparing food and plant products with the Waring Blendor, and the limitations of this equipment, have been discussed in three recent papers (*90, 131, 148*).

Recently, so-called ethylvanillin is being used to reinforce vanilla extract because its flavor strength is greater than that of vanillin. In this connection, methods have been suggested for estimating vanillin and ethylvanillin in vanilla extracts (*12, 158, 181*).

A "chromatostrip" has been devised for the separation and identification of terpenes, especially as they occur in citrus oils (*97*). The strip is prepared by coating a glass strip with a slurry of silicic acid absorbent, starch binder, and a zinc-cadmium sulfide complex plus zinc silicate fluorescing agent. An improved manometric technique has been developed for evaluating the oxidative stability of cold pressed orange oil (*94*). The procedure permits determination of the true oxygen uptake of the oil. During oxidation, carbon dioxide and water are evolved, and because these interfere with the measurement of oxygen absorbed, they are removed, thus giving more realistic stability values.

The usual method of determining essential oil in orange juice is by distillation. A nephelometric method suggests mixing the juice with acetone and then distilling (*53*). By shaking an aliquot part of the distillate with water, a turbidity is produced that is compared with suspensions of essential oil of known concentrations. The method cannot be used if the oil content is below 0.1 ml. per liter.

The respiration rates of microorganisms in orange juice has been proposed as a possible index of population (*81*). Laboratory studies have indicated a relationship between oxygen consumption and microbial population.

A rapid method for determining betaine, one of the principal noncarbohydrates in sugar-beet processing liquors, consists of precipitating crude betaine reineckate from a hydrochloric acid solution (*179*). The purified reineckate is converted to the soluble nitrate and the determination completed by titration. Of interest, too, is a method for estimating trigonellene, the methylbetaine of nicotinic acid, in coffee (*129*). Trigonellene represents about 5% of the soluble solids in coffee beverage and contributes to coffee flavor and aroma. It may also have physiological properties.

Other methods of interest to food analysts are determination of benzoic acid in preserves (*74*), rapid test for chocolate temper (*54*), determination of alcohol without distillation (*100*), and proposed standards for scoring and measuring open egg quality (*18*).

A portable instrument for determining ethylene in air (*170*) should be of interest to technologists associated with fruit processing, and a recording Warburg manometer (*4*) should be useful to biologists and chemists using this instrument. A new shear press, operating on Tenderometer principles, for quality of lima beans, has been described (*99*), and from Australia comes the Maturometer (a form of Tenderometer) for testing the maturity of peas (*60*).

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SOLID AND GASEOUS FUELS

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THIS third review of the analysis of solid and gaseous fuels continues former reviews (*23, 38*) and includes a bibliography of references found from September 1949 through September 1951. The arrangement follows closely that of the other reviews.

SOLID FUELS

This section discusses the sampling, testing, and analysis of such fuels as coal, coke, wood charcoal, and briquets.

SAMPLING

Sanchez (*102*) reviews the standard methods of sampling used in various countries with a view toward developing a standard method for Spain. The methods in use in Spain are described in detail (*103*).

PROXIMATE ANALYSIS

Zanki and Schwabe (*128*) have tabulated proximate analyses of Ruhr and Saar coals made in 1949 and 1950.

Volatile Matter. Shakhno (*110*) found that the usual methods for the determination of volatile matter in coals do not give accurate results because the temperatures are not high enough to drive off all the volatile matter. Heating to 1200° C. is necessary to ensure complete volatilization. The methods used by him are described and the data obtained are reported for a number of Russian coals.

Aranda and Sanchez (*4*) review methods for determination of volatile matter using a gas burner or a muffle-furnace as used in various countries. The method consists of heating a 1-gram sample in a muffle at 950° C. for 7 minutes. Samples that decrepitate are heated 5 minutes at 450°, then 6 minutes at 950°. The dimensions of the porcelain crucible (40 mm. in top diameter, 38 mm. high) and cover are given in detail. Reproducible results are shown for seven samples of from 2 to 42% volatile matter.

Ash. Mukherjee and Dutta (*81*) report spectrographic analyses of the ash of coals from various parts of India. Germanium and gallium were present to a considerable extent in some coals.

Edgcombe *et al.* (*28*) describe the principal changes in previous methods of ash analyses. The preparation of the ash is devised to avoid preparation from thin layers of coal. A procedure for dissolving the ash allows for the solution of all ashes examined. A simplified and shorter method for separating silica and a simple method for determining barium are given. Iron and titanium are determined without previous separation. Platinum obtained from contamination by laboratory apparatus is removed, then magnesium, manganese, phosphorus, sulfur, and alkalies are determined. The analytical procedure is described and a list of required reagents is given (23 references).

Aranda and Sanchez (*4*) discuss the nature of the ash in coal as well as the reactions occurring during ignition. In experiments on ash determination, a gas burner was found unsuitable owing to variations in gas supply and heating value. In the accepted method the air-dried 1-gram sample was heated in an electric muffle furnace 0.5 hour at below red heat, 0.5 hour up to 500° to 600°, and 3 hours at 800° with subsequent 0.5-hour ignitions to constant weight. The crucibles used successfully are shown in cross section. Typical results from over one thousand determinations on various coals and lignites of from 2.6 to 42.6% ash are given.

Hunter and Headlee (*58*), in a spectrographic method of analysis of coal ash, grind the coal to 200 mesh and mix well. A 5-mg. sample is placed in a graphite electrode and heated for 10 minutes at 550° in an electric muffle to drive off volatile matter. The samples are run as the positive pole of a 220-volt direct current arc and burned to completion. A logarithmic step sector is used with each exposure. Densitometer readings of spectrum lines in a known sample are compared with those of a chemically analyzed sample run on the same plate, thus yielding a quantitative analysis. The chemical analysis of the standard was checked against a synthetic standard. Analysis included oxides of silicon, iron, aluminum, titanium, calcium, magnesium, sodium, and potassium. Data are given on comparative analyses of wet and spectrographic methods on 70 samples. Results of these two analyses of ash content are found to check within 1% in 97% of the tests, but systematic differences are found for several of the oxides.

Lifshits (*70, 71*) gives a simplified method for ash determination, which he claims is satisfactory as a control method at the mine. A 2- to 10-gram sample ground to 1-mm. size is weighed to about 0.01 gram and coked on a 50 × 80 mm. tray in a thin layer in a preheated muffle at 850° to 900°. Wet samples are dried at 105°.

Myhill (*82*) discusses the latest information on method of ash analysis.

Beugou and Conjeaud (*16*) describe the laws of absorption of x-rays in coal. Apparatus for producing and using x-rays in irradiating specimens and the preparation of specimens are described. Arrangements for testing were developed. The accuracy is about 0.5%.

Ash Softening Temperatures. Radmacher (*97*) describes a new ash-fusibility apparatus developed by Leitz (*77*) which permits the entire fusion process to be followed and recorded photographically.

> Ash prepared by ignition at 775° ± 25° C. is ground in an agate motor and reheated to 775° until it all passes through a test sieve. It is then slightly moistened and formed into a cylinder 7 mm. in diameter and 7 mm. high in a special hand press. Ash requirements are about 0.3 gram. This test piece is then placed on a refractory plate and introduced into an electric or gas-fired furnace at 800°. Temperature is increased at 5° per minute for an oxidizing atmosphere and 3° to 4° per minute for a mixed atmosphere. For photographic records of the ash-fusion behavior a special electric furnace is provided with a gas-tight tube provided with quartz windows. A special microscope is used for observing the specimen and is provided with a special plate on which a grid is etched. Provision is made for attaching a camera of the Leica type. Either transmitted or reflected light can be used for observations and photographs.

Typical photographs are shown of the behavior of ash fusion samples during heating.

Moisture. Aranda and Miranda (*5*) review various methods of moisture determination:

A. Drying at 105° C.
B. Drying in vacuum over a desiccant
C. Drying in a current of inert gas followed by recovery of water by calcium chloride and weighing
D. Gasometric methods using methyl magnesium iodide, calcium carbide, etc.
E. Cryohydric method of Dolch
F. Dielectric methods
G. Distillation with an immiscible solvent

Their results on seven samples containing from 1 to 31% moisture comparing methods A and E find fair agreement, E giving the higher result in all cases but one. Nine samples of Spanish lignite were used in testing method A with or without a current of air or inert gas, and in testing methods B, C, and G. A was considered unsatisfactory with samples of such great absorptive power. B was too slow, requiring several days. C or G was considered satisfactory, toluene serving as well as xylene in G.

Barber (*6*) also reviews several methods for determining moisture and discusses some of the difficulties encountered. Accurate sampling of wet products is made more difficult by the uneven distribution of moisture in the batch or consignment. He concludes that duplicate sampling is probably desirable and that subsamples and control charts are necessary adjuncts to a proper appraisal of the moisture content.

Asbach (*5*) describes a continuous method for the determination of moisture in coking coals. An electric condenser system in which the change in capacity is correlated with the moisture content of the coal by means of the resulting change in dielectric constant of the surface condenser is obtained by mounting the surface condenser in a chute down which the coal passes. The results are in very good agreement with those obtained in a drying oven over the range of 8 to 14% moisture.

Calorific Value. Cossey (*22*) describes an automatic water feed for maintaining the water level in the Cutler-Hammer recording calorimeter tanks by the use of an auxiliary brass reservoir in which a 5-gallon bottle of water can be inverted.

Botló (*18*) discusses several formulas for the calculation of calorific value of coal and has worked out a practical formula, making the assumption that a part of the temperature curve can be replaced by a straight line from the beginning of combustion. Heating value is calculated from

$$C = m \times \Delta v - (t_k - t_0) \times (\Delta c + \Delta v)/(t_2 + t_4)$$

where m is the time in minutes during the main measurement, Δv the mean temperature of secondary measurement, Δc the mean temperature of the preliminary measurement, t_k the mean temperature of total experiment, and t_0 the temperature increase of medium in a minute. The formula gives values with deviations of 4 to 6% when compared with the results obtained by the Regnault-Pfaundler formula.

Abramski and Grumbrecht (*1*) propose a new formula for calculation of the calorific value of low rank coals on a moisture- and mineral-free basis.

$$\text{Kg.-cal.} = \frac{100[\text{kg.-cal. found} - 31.65(S - 0.8)\}}{[100 - (1.1A + 0.5S - 0.4)]}$$

In this formula $31.65(S - 0.8)$ represents the heat of combustion of pyrite sulfur, while the factor 1.1 is applied as a correction for the water of hydration retained in the ash, A. In the denominator $0.5S - 0.4$ represents a factor for organic sulfur. S and A are expressed in percentages. Experiments show good agreement with values calculated by the proposed formula.

Schuster (*109*) tested some of the equations suggested for estimating the heating value of coal from the proximate analysis. The analytical results for 117 coals reported by Sacy and Bonnal were used. The formula $H_0 = 59.4K + B(267.4 - 3.85B')$ gave the best correlation; in this formula H_0 = calorific value of the raw or dry coal in kilocalories per kilogram, K = per cent pure coke in the raw or dry coal, B = per cent volatile matter in the raw or dry coal, and B' = per cent volatile matter in the pure coal. A rough correlation was shown to exist between the volatile matter on a pure coal basis and the tar yield (pure coal basis) and gas density, etc., but the correlation was less good between volatile matter and water of decomposition, which should be determined directly.

Schuster (*108*) compares graphically five published formulas for calculating the heating value of coal from the proximate analyses. The two giving the best results over the range of 18 to 40% volatile matter are $H_0 = 8070 + B(66.5 - 1.65B)$, kg.-cal./kg. (*55*) and $H_0 = 8000 + B(70 - 1.65B)$, kg.-cal./kg. (*108*). Both formulas are based on ash- and moisture-free coal, and B is the percentage of volatile matter or $(100 - \%)$ = pure coke.

ULTIMATE ANALYSIS

Carbon and Hydrogen. Duffy (*27*) describes a graphical method for total carbon based on an empirical formula relating proximate analysis, sulfur content, and calorific value. A nomograph employing these data, with an accuracy of 0.28%, is given for use with bituminous coals.

Belcher and Ingram (*10*) describe a new type of combustion apparatus which uses the empty tube technique and in which a combustion can be completed in 10 minutes. The combustion zone of the tube consists of a vertical double-walled chamber heated by a special kind of split furnace. The purification train has been specially designed to permit easy replacement of reagents without interruption of the oxygen stream. Sulfur oxides and halogens are absorbed on heated silver gauze, and nitrogen oxides are taken up by an external absorbent of granulated manganese dioxide (*11*). The whole assembly, exclusive of three absorption tubes, occupies a bench space of 51 × 23 cm.

Nizovtsev (*86*) gives a description, with diagram, of an improved alkali-absorption bulb for carbon dioxide determination, embodying the use of two internal floating valves (glass) which simplify construction and operating by eliminating any residual gas bubbles in the apparatus.

British Standards Institute (*19*) specifies all necessary components of the carbon and hydrogen combustion trains with dimensions and drawings, together with the quality of the glass combustion tubes and rubber tubing.

Wagner (*126*) modified somewhat the combustion tube for carbon and hydrogen determination and provided two readily exchangeable extension tubes. To obtain good hydrogen values it is recommended to burn samples free of nitrogen without any lead dioxide in the combustion tube and to use lead dioxide in the extension tube when nitrogen is present. Absorption tubes that can be closed with wires are used and are not wiped between the removal of the tubes and the weighing. The addition of a little magnesium perchlorate to the ascarite prevents premature clogging of the tube used for absorbing carbon dioxide.

Nitrogen. Noyce (*88*) proposes a modification of the conventional Dumas apparatus that can be easily assembled from common chemical laboratory items and reduces to one half the time required for the usual macroprocedure. Essential features include a convenient carbon dioxide source, use of a back-flush technique, and a means for cooling the combustion tube outside the furnace. Samples of 0.10 gram or less have been used satisfactorily.

Johanson (*61*) describes a system of readily constructed conical glass bells that fit over the top of the mouths of Kjeldahl flasks. The bells are connected flexibly to a common vacuum off-take, eliminating the need of a fume hood.

Blom and Schwarz (*17*) describe a method for the direct titration of ammonia in Kjeldahl determinations. $NiSO_4.(NH_4)_2SO_4.6H_2O$ is used as the absorbent.

Sulfur. Hamaker (*49, 50*) discusses the method devised by Hambersin (*51*) and Pieters and Popelier (*92*) for the determination of sulfur content of fuels and compares results on nine samples with results by the Eschka method (*93*).

Kurchatov (*66*) describes a method for the determination of the inorganic (ash) sulfur in coal and coke.

Samples of 15 grams of ash were placed in a 250-ml. Erlenmeyer flask, then mixed with 20 ml. of 3% hydrogen peroxide and heated a few minutes with a low flame. Concentrated hydrochloric acid (1 ml.) was then added to the mixture and heating continued a few minutes. The mixture was diluted with 80 ml. of water and 6 grams of ammonium carbonate were added. The flask was then covered with a watch glass or preferably with a glass stopper drawn out to a capillary. The flask was again heated until the carbonate was completely decomposed. The contents of the flask were diluted with boiling water, filtered, and washed. The filtrate contains the sulfur as ammonium sulfate and the sulfur was determined by precipitation as barium sulfate in the usual manner.

A second method (*67*) is given in which samples of ash (from 0.2 to 0.5 gram) were well mixed with 1 gram of zinc powder and 1 gram of mercuric chloride, then placed in a porcelain crucible. The mixture was covered with zinc powder, and the crucible was covered, then heated 20 to 25 minutes over a Bunsen burner. The crucible was cooled, then placed in a wide-necked flask where

> the contents of the crucible were decomposed with hydrochloric acid in a stream of carbon dioxide. The flask containing the crucible also contained water to a level above the height of the crucible. The flask was heated, thus driving off hydrogen sulfide, which was collected in a mixture of cadmium acetate and acetic acid. The cadmium acetate solution was titrated with standard iodine solution. This method was applicable to ash of low or high sulfur content.

Chernyǐ and Podoinikova (*20*) determined the total sulfur in coal and coke by grinding a 0.2-gram sample with 1 gram of metallic calcium and 3 to 4 grams of dry oxalic acid, heating in a boat in a 750° to 800° C. tube furnace in a carbon dioxide stream, and collecting the hydrogen sulfide in a three-bulb system of cadmium acetate–acetic acid absorption mixture. Titration of the bulb contents with iodine–sodium thiosulfate gave the sulfur content to an accuracy of 0.03%.

Conner (*21*) finds that in the Parr peroxide bomb method for the determination of sulfur the 0.3 gram of benzoic acid usually used in the oxidizing mixture may be efficiently replaced by salicylic acid.

Mott (*79*) shortens the time required in the older method of determining the forms of sulfur that exist in a coal. Sulfur exists in coal in the forms of sulfate, pyritic, and organic sulfur, of which perhaps the most important is the pyritic sulfur, usually high in high-sulfur coals. Organic sulfur is obtained by the difference between the total sulfur and the sum of the sulfate and pyritic sulfur. The present standard method for determining sulfate and pyritic sulfur in coal requires digestion for 40 and 24 hours, respectively, in dilute hydrochloric acid and dilute nitric acid at 60°. The new method reduces the digestion time to 30 minutes for each acid that is boiled. Results agree well with the older method.

In extracting sulfate sulfur from coal, 16% hydrochloric acid is used at the boiling point for 30 minutes (*80*). All the pyrites are removed by boiling coal for 30 minutes with 2 *N* nitric acid.

Šimek, Helm, and Koštál (*45, 114*) determined the free sulfur in coal or coke by extracting a 10-gram sample with benzene at 78° C. or with carbon tetrachloride at 60° for 24 hours. Hydrogen sulfide is removed by shaking with cadmium chloride or acetate and free sulfur is precipitated by shaking with mercury. Mercuric sulfide is dissolved in aqua regia and the resulting sulfuric acid is determined as barium sulfate.

Bartoň and Střížová (*8*) found that when oxygen was passed over the sample in a quartz tube and at a combustion temperature of 1000° in the presence of carbonates of calcium, manganese, and magnesium, the sulfur was not completely recovered using the Grote-Krekeler procedure (*46*). The sulfur left in the residue was determined separately.

Belcher and Spooner (*13*) have modified their rapid method for the simultaneous determination of carbon, hydrogen, sulfur, and chlorine in coal (*12*). Carbon and hydrogen are determined as in the original method, but sulfur is determined by titrating the silver sulfate extracted from the silver gauze with standard potassium sulfocyanate solution. This modification enables rapid and convenient determination of carbon, hydrogen, and sulfur in a series of coals by a single combustion.

Barthel, Herglotz, and Lissner (*7*) determine the total sulfur in solid fuels by burning a sample of the fuel in a calorimetric bomb to convert the sulfur to sulfate, which is determined by conductometric titration with 0.1 *N* barium acetate solution.

Mott (*78*), to determine the pyritic and sulfate sulfur in a coal, grinds the sample to 72 mesh and extracts by boiling with 16% hydrochloric acid for 30 minutes, thus removing nonpyritic and sulfate sulfur. Another sample is extracted with 2 *N* nitric acid by boiling for 30 minutes, removing the pyritic sulfur. Iron is determined on the nitric acid extract, and then the nonpyritic iron in the hydrochloric acid extract is deducted to calculate the pyritic sulfur as FeS_2.

Phosphorus. Radmacher and Schmitz (*98*) developed a rapid and accurate photometric method for the determination of phosphorus in fuel ash based on the phosphomolybdenum blue method of Tschopp and Tschopp (*121*). Sources of error were investigated and substantially eliminated. Details as to reagents and procedure are given (*98*).

Belcher (*9*) developed a method for the determination of phosphorus in coal and coke which requires less than 2 hours. Phosphorus is extracted from the ash as described in British Standards No. 1016, except that smaller amounts of ash and acid are used. The phosphorus is finally determined by the development of molybdenum blue, the color intensity of which is measured in a Spekker absorptiometer. Fifty milligrams of ash are used, regardless of the phosphorus content. This amount of ash may normally be obtained from that remaining after determining the ash content.

Oxygen. Mantel (*75*) determined the amount of oxygen in a number of low-ash Ruhr coals by calculation from the laboratory carbonization products: aqueous condensate, carbon monoxide, carbon dioxide, and the oxygen in tar and coke. When the percentage of volatile matter (pure coal basis) was plotted against the oxygen percentage, a smooth curve resulted. This was also true when the ratio of oxygen to volatile matter was plotted against volatile matter. The low point on this curve (around 19 to 20% volatile matter) corresponded to the minimum volatile matter content of a coal that will form a good solid coke.

Harris, Smith, and Mitchell (*52*) reported a new technique for the direct determination of oxygen in organic compounds based on the Unterzaucher method (*122*). The sample is decomposed in a stream of helium and the pyrolysis products are circulated in a closed system over carbon at 1100° until all the oxygen is converted to carbon monoxide. During the circulation practically all of the hydrogen is removed selectively by diffusion through a heated palladium tube. The procedure permits the use of large samples and as little as 0.1% oxygen can be determined. The composition of the resulting helium–carbon monoxide mixture is determined with a thermal conductance bridge with a sensitivity of 0.20% carbon monoxide per mv. Continuous recording of bridge potential is employed; this gives a means of following the pyrolysis.

Miscellaneous Tests. Golumbic *et al.* (*42*) report that extraction of a bituminous coal with phenanthrene at 340° and examination of fractions of the recovered extract by x-ray powder photography yielded a characteristic diffraction pattern, which was identical with that given by partly amorphous abietic acid and aluminum and ferric abietates. No reliable estimate of the concentrations of these constituents could be made, but qualitative observations indicated that they are minor constituents.

Thomas and Wilkinson (*118*) determined carbon dioxide in coal by adding 10 ml. of 5 *N* hydrochloric acid and measuring the pressure increase in an apparatus of constant volume, which had been standardized with sodium carbonate. No effective difference is caused by more finely grinding the coal, so that 72-mesh British Standard is satisfactory. The short period of heating or strength of acid used does not produce hydrogen sulfide or release occluded methane.

Parks (*89*) determined the banded ingredients, particularly vitrain and clarain of broken coal from several Illinois coal mines, by identifying and counting coal particles in selected samples. The petrographic technique and the analyses are described.

Wainer (*127*) describes the use of the Rockwell-Bullens calculator for computing the relative economic values of fuels.

Hubáček (*55*) studied the humic acids in coal. The principle of base exchange is adopted from Fuchs (*35*).

> One gram of powdered coal is washed with water and treated with sodium acetate to convert free acids and their salts to sodium humates. Portions of the filtrate are titrated with potassium hydroxide to determine free humic acids and iron. Calcium and magnesium are determined in acidified portions and calculated to the corresponding humates. Aluminum is negligible and is determined along with iron. Dissolved calcium sulfate in the filtrate may give high results for calcium humates and is corrected by a

sulfate determination. Total humic acids are determined by treating the sodium humates with barium acetate solution and noting loss of barium in the filtrate.

Spooner (*115*) reviews and discusses micromethods, sampling, and proximate and ultimate analysis of coal and gas.

Niezoldi (*85*) critically reviews the sources of error in coal sampling and points out relatively large errors occurring in practice. In sampling, special care must be taken to avoid segregation or moisture loss. Sources of error in heating value determinations are pointed out.

Plastic Behavior on Carbonization. Kreulen (*65*) investigated the British Standard 1016:1942 [identical with A.F.N.O.R. (French Standard) M11001:1944 and A.S.T.M. D 720-46, swelling test of coal]. The profiles that accompany the standard procedure refer partly to conditions which are unrealizable with the normal crucibles used. The swelling number fails completely as an index for the evaluation of the coking properties of a coal or as a classification index. During the oxidation the swelling number of certain ordinary coal types passes through a maximum. The existence of this maximum is illusory; it is in fact due to a lag in swelling of the freshly prepared coal sample under the conditions of the test. This lag results from a collapse of the coke button consequent on too low a viscosity of the plastic mass during its formation. Some evidence has been found that the stability of a coal on storage might be derived from the progress in swelling number during oxidation at a higher temperature (100° to 125°). The procedure, however, is rather cumbersome and similar information might be obtained along other lines.

Förch (*32*) discussed British Standard coal swelling test 1016:1942 and compared its results for a number of coals with the "Amsterdam scale" for swelling index. The latter was developed for use with coal in vertical ovens and is based on the size of the coke button obtained from ordinary volatile determination in a platinum crucible. The Amsterdam method is found more rapid and useful. A graphical and photographic presentation is given.

Gehle (*40*) determined the caking, swelling, and expansion tendencies of a coal in single test. Use is made of a previously suggested caking test (*39*) with a quartz dish 20 mm. deep and 45 mm. in diameter with certain modifications to increase accuracy. Instructions are given for introducing the sand and coal layers into the dish, which is then covered and held at 850° until flames disappear. The dish is then removed, cooled without the cover, and reweighed. A sand-displacement method is given for determining swelling. Strongly swelling coals give a coke button of dish-shaped contour, especially with certain ratios of sand to coal. This shape and the swelling measured by the sand-displacement method have been roughly correlated with the expansion pressure. Examples of the data obtained and calculation required are given. Test results indicate that for a given coal increasing ash content and extreme fineness cause an increase expansion pressure.

Kozina, Herda, and Svĕtný (*64*) applied the Sapoznikov method for evaluation of coking coals to the determination of the quality of Ostra-Karvin coals. In principle, Sapoznikov measures the quantitative expansion and subsequent reduction of a tested coal upon heating in an electric furnace.

A coal charge of 100 grams is placed in a large steel crucible. The top of the coal is held under a pressure of 0.6 kg. per sq.cm. with a perforated lid. The perforated bottom of the crucible is lined with asbestos paper and the sides with filter paper. The coal has to pass through openings below 1.5 mm. Protected thermocouples are inserted to the bottom and provision is made to insert a steel needle during coking experiments. The heat is applied to the bottom of the crucible, so that 250° is attained in 50 minutes, and the crucible is heated at the rate of 3° per minute. The experiment is terminated when a temperature of 730° is reached. Actual measurements are made between 250° and 650°. The changes of the top and bottom layers are recorded and plotted on two separate diagrams. The recording is done by means of the needle connected to a drum rotated by a clock mechanism. The first diagram furnishes the maximal vertical expansion; the second diagram, volume changes *vs.* time; and from a series of these determinations a third diagram is plotted which serves for classification purposes.

GASEOUS FUELS

CONVENTIONAL ANALYSIS

Gooderham (*43*) further developed a previously described method of gas analysis, with a series of absorbers and soap bubble gas meters. Carbon dioxide, oxygen, hydrocarbons, hydrogen, carbon monoxide, and paraffin hydrocarbons are removed successively from coal gas, so that only nitrogen and other inert gases are left flowing in the last meter. The apparatus can also be used for determining the carbon density of unsaturated hydrocarbons. Changes from earlier apparatus include the methods of bypassing the meters and of forming the soap films. The use of solid reagents for oxygen and carbon monoxide has made it possible to develop more convenient portable apparatus for determining these constituents.

Fastovskiĭ and Rovinskiĭ (*30*) describe an alternating current potentiometer-type apparatus for the flow-method determination of the heat conductivity of gas mixtures. Calibration curves for some binary gas mixtures are given.

Gruzdeva (*47*) gives a method of preparing colloidal palladium for the determination of hydrogen in gases.

Add 500 grams of fresh egg white to 550 ml. of 3% sodium hydroxide with stirring, heat 2 hours at 60° to 65°, filter, add acetic acid until acid, filter, wash the precipitate with a little water, stir into a paste with water, dialyze in cellophane against water for 2 days, neutralize with 10% sodium hydroxide until clear, again dialyze until neutral, and concentrate to a small volume at 50° to 60° C. Dry in a vacuum desiccator over calcium chloride; the resulting sodium protalbinate is a very stable protective colloid. To 4 grams of the colloid in 70 to 80 ml. of water add a 10% excess of 10% sodium hydroxide and slowly add 4 grams of palladium chloride, add 80 to 90 ml. of 0.15 *N* hydrochloric acid while stirring, and reduce the red solution with hydrazine added in 25% excess; after 3 hours dialyze the palladium colloid until free of chlorine, evaporate at 60° to 65°, and finally dry in a vacuum over calcium chloride. In this way black friable particles are obtained which are readily peptizable in water. To 6 grams of the preparation in 100 to 150 ml. of water add 7 grams of picric acid in 30 to 40 ml. of water, neutralize with 34 ml. of 1 *N* sodium hydroxide, and use the solution in conventional gas-absorption bulbs for hydrogen uptake.

Glogoczowski (*41*) determined the helium content of natural gas after absorption of the other constituents with activated carbon at the temperature of liquid air.

Towler and Wood (*120*) determined the unsaturated hydrocarbons in fuel gases, using a Bone and Wheeler apparatus with a constant volume space of about 75 ml. by means of sulfuric acid activated with 0.6% silver sulfate or 0.2% chromium trioxide. The methods of preparing these activated acids are given.

Shepherd (*111*) compares two volumetric methods of absorption-combustion by studying the results of the analysis of a standard sample of the natural gas type.

Method A depends upon the measurement of contraction on burning and the carbon dioxide produced. Method B adds to these the measurement of oxygen consumed. Method B gives greater accuracy in the determinations of carbon dioxide, oxygen, nitrogen, methane, ethane, calculated heating value, and calculated specific gravity. It yields greater reproducibility in the determination of carbon dioxide, oxygen, and nitrogen and in calculated heating value. Method A gives greater reproducibility in the determination of methane and in calculated specific gravity. Reproducibility is about the same in the case of ethane. The results of Method B can be made to agree with those obtained by the mass spectrometer, but this is not true for Method A.

Luszczak (*73*) describes an analytical process based on the measurement of the height of the green cone of a specially constructed Bunsen burner supplied with a regulated flow of coal gas. The method gives the content of oxygen, and of combustible gases and vapors, as well as the approximate carbon dioxide content of the gas mixture. The mixture to be investigated is passed into the burner mixed with a measured quantity of oxygen as primary air. Large quantities of hydrogen (10%) and also considerable quantities of carbon monoxide do not interfere, as they act like inert gases, so that methane can be determined in gas mixtures, such as the exhaust gases from internal combustion engines. The method can be used to determine directly the air ratio necessary for the complete combustion of hydrocarbon vapors in internal combustion engines.

Procházka and Klíma (*96*) modified Kattwinkel's apparatus (*63*) to determine the efficiency of plant benzene scrubbers. Benzene was absorbed on activated carbon. The accuracy of this method was ascertained by absorption of a known weight of benzene. A correction factor of 0.6 ml. had to be applied. A minimum of 300 liters of rich gas or 2000 liters of lean gas was required; the gas could be moist. Naphthalene or a small quantity of higher hydrocarbons does not interfere. During a 24-hour test this method furnished results comparing favorably with the freezing-out method or actual plant yields.

Prchlík (*94*) gave methods for the determination of oxygen, hydrogen sulfide, and benzene in illuminating gas by polarographic analysis.

> For the determination of oxygen in concentration of 0 to 1.0%, the gas is passed through a solution of lithium chloride in methanol, which has an oxygen absorption coefficient 7.1 times greater than water. The equilibrium concentration of oxygen in methanol is used as a standard. For the determination of hydrogen sulfide on the order of 2 to 5 grams per cubic meter of gas, advantage is taken of the depolarizing effect of sulfide ion in polarographic electrolysis caused by the precipitation of mercuric sulfide. In the presence of oxygen, the cathodic wave of oxygen adds to the anodic wave of sulfide ion to form a resultant wave. The reduction of the oxygen wave in 0.1 *N* sodium hydroxide is used to indicate hydrogen sulfide concentration. Benzene is first absorbed in a nitrating mixture and converted to nitrobenzene, which is determined polarographically against a standard nitrobenzene standard.

APPARATUS

Hooper *et al.* (*54*) give details of the standard Orsat apparatus used in the petroleum industry. Combustion methods and sources of error are discussed.

Fry, Burton, and Edholm (*34*) describe in detail a simple, inexpensive gas analyzer. An analysis requires about 5 minutes and the probable error of a single determination is about 0.05% when the gas measured is 20% of the total volume of the sample.

Stover, Partridge, and Garrison (*116*) describe an apparatus and method for microanalysis based on the Saunders-Taylor (*105*) and Garrison and Burton (*37*) methods. The apparatus is simplified by the use of standard stopcocks and ground joints, which makes it easier to build and to keep in operation.

Faĭnberg (*29*) describes, with photographs and diagrams, automatic and semiautomatic commercial models of gas analysis apparatus, largely European.

Pozzi-Escot (*93*) describes a simple apparatus for industrial gas analysis.

Peregud (*91*) describes visual type of colorimeter. It consists of a small absorption bulb into which the gas can be directed from the sample pipet; the bulb is filled with approximate indicator solution and the color secured is matched visually against a color concentration scale standard. The following are recommended: safranine for nitrogen tetroxide, auramine for chlorine, fuchsin for aldehydes, methyl violet for methanol, methyl violet–safranine for benzene, and auramine-safranine–brilliant green for hydrogen sulfide.

Vasserberg and Zhabrova (*124*) describe an apparatus suitable for gas analysis in the field. It utilizes a combustion tube filled with suitable catalyst, which is wrapped with platinum or palladium asbestos, heated preliminarily by ignition of some alcohol poured on it, then inserted into a can containing some methanol; the continued combustion of methanol vapor on the catalyst maintains 280° to 300° within the combustion tube, which can be raised to 400° by forcing air from bellows into the combustion chamber.

Hartree and Harpley (*53*) describe a mercury gasometer for making up accurately two gas mixtures to 1500 ml. It is especially suitable for mixtures containing a very low proportion of carbon monoxide or oxygen.

Schmidt (*106*) makes successive measurements of gas volumes during an analysis with a glass diaphragm-type compensator. This compensator and method of measurement have the advantage of minimizing the possibility of mixing gases, together with an audible control of the pressure balance in the analyzer system. In its present form, the compensator consists of a small glass ball flattened by heating one portion of it so as to give a wrinkled surface. This surface, under a pressure of a few millimeters, will click and upon release of the pressure will again click as it returns to its original setting. Instructions are given for making and using this device as well as the manometer-compensator.

Ioffe and Shvarts (*60*) give structural details of a gas analyzer of the Orsat type.

Reed (*101*) describes a portable unit for gas analysis that requires only a supply of circulating water and gas or electricity for furnace heating; it is readily dismantled and reassembled. Pressure variations on the water-jacketed constant-volume chamber are secured by means of a bellows (operated with a hand wheel) filled with 90% glycerol and 10% water, which exerts pressure on the mercury used as the displacing liquid. A movable reservoir is also provided for rapid movement or gas to or from the constant-volume bulb.

Gruzdeva and Krivousov (*48*) describe an automatic absorption vessel for gas analysis, which is provided with a perforated glass distributor plate and an up-down magnetic stirrer. Time saving over conventional bulbs is claimed.

Bertein *et al.* (*15*) used photoelectric analyzers for the determination of colored gases. RCA tubes 929, 934, and 926 were used to determine and record automatically the chlorine or nitrogen dioxide content of a gaseous mixture, to determine humidity of a gas, to indicate passage of a quantity of one of these gases, and to permit immediate stopping of circulation of all gases.

Fréling and Dugleux (*33*) discuss the operation and accuracy of a new all-glass gas analysis apparatus that has a measuring unit of constant-volume type. Water vapors are absorbed by magnesium perchlorate, carbon dioxide by ascarite, and oxygen by Hopcalite; carbon monoxide and hydrogen are selectively oxidized by cupric oxide.

Dobrinskaya, Neĭman, and Andreev (*25*) describe a microanalytical apparatus capable of handling accurately 0.001 ml. The liquid mercury closure and solid absorbents are used in the usual analytical procedure for the common constituents.

Schmitt (*107*) describes an apparatus that is new but based on previously used techniques. Determinations accurate to 0.001 volume % of carbon dioxide, carbon monoxide, methane, and hydrogen sulfide are made by measurements of the change in electrical conductance of a barium hydroxide solution upon its reaction with carbon dioxide or sulfur dioxide of a gas sample. With carbon monoxide and methane the gas sample is oxidized to carbon dioxide and then passed into the barium hydroxide. The apparatus and its operation are described in detail; the apparatus has been developed to furnish fast analyses of 50 to 100 cc. of sample.

Reed (*101*) found that when the Orsat apparatus is used to adjust fuel burners to definite carbon dioxide readings, the presence of excess oxygen in the combustion products must first be checked, as high carbon dioxide reading may also occur with a slight air deficiency. Solutions must be replaced periodically, as they lose absorbing ability, and operating instructions must be followed. Sample lines must be tight and the Orsat apparatus must be constantly checked for leakage. If the flue gas temperature is over 800° F., the sample should be taken through a water-cooled sampling tube.

Donnelly and Broadbent (*26*) report some modifications to Gooderham's continuous-flow-type gas analysis apparatus (*44*). Nichrome and aluminum wire is substituted for glass rod in making the helixes of the gas scrubbers. The use of solenoid soap film makers is described and constructional details are given. The order of accuracy and repeatability of the analysis is better than 0.5%. The apparatus is adaptable over a wide range of gas compositions, some of which are infrequently reported.

Carbon Monoxide. Lindsley and Yoe (*72*) describe an instrument which, operating continuously, will indicate when certain specified concentrations of carbon monoxide are present in the air drawn through it, by oxidizing over Hopcalite and measuring the rise in temperature. Specially designed thermometers, having platinum contacts in the stems at intervals corresponding to the desired gas concentrations, activate appropriate signaling devices when the circuits are closed by the rising thread of mercury. A limitation exists in the fact that only ranges can be shown and only a limited number of contacts can be incorporated in the thermometer.

Prchlík and Otta (*95*) designed a gas-absorption apparatus to avoid some of the disadvantages of the iodine pentoxide method for the determination of low concentrations of carbon monoxide. They used a modified combustion method.

> The gases are measured in a 1000-ml. gas buret containing saturated sodium sulfide as confining liquid. The gases enter a scrubber with 30% potassium hydroxide to remove carbon dioxide and a safety wash bottle with 0.005 *N* barium hydroxide and then are led over granular refractory material 3 to 10 mm. in size in a Mars-tube furnace held at about 900°. The products of combustion, with formed carbon dioxide are absorbed in a series of three wash bottles, each one containing 20 ml. of 0.005 *N* barium hydroxide. After the run the excess barium hydroxide is titrated back with 0.005 *N* oxalic acid to phenolphthalein.

Toensing and McKinney (*119*) modified the combustion-absorption procedure for determining carbon monoxide and carbon dioxide in gas mixtures so as to give a precise determination of large amounts of carbon monoxide. A 500-ml. sample is passed in all-glass apparatus over cupric oxide at 700° to convert the carbon monoxide to carbon dioxide and through Anhydrone and Ascarite. The sample is flushed through the apparatus with oxygen. Ascarite absorbers are weighed to 0.2 mg.

Carbon Dioxide. Bennett (*14*) developed a new technique for rapid and continuous estimation of carbon dioxide. A current of the dried gas is aspirated through a Napier Shaw pneumatic bridge circuit with the addition of an absorption vessel of suitable design in one limb of the circuit. When potassium hydroxide solution is fed into the vessel, any carbon dioxide is absorbed, and the volume of the gas flowing through the second resistance in the limb is reduced. If the circuit has been initially balanced on carbon dioxide–free air, the pressure difference shown between the mid points of the two limbs of the circuit is a direct and quantitative measure of the amount of carbon dioxide removed.

Nieuwenburg and Hegge (*84*) recommend the use of a solution of barium hydroxide in a mixture of aniline, ethanol, and water, instead of the usual water solution for the quantitative absorption of carbon dioxide. This does away with the large excess of barium hydroxide and with complicated absorption apparatus.

Sulfur. Sands *et. al.* (*104*) determined low concentrations of hydrogen sulfide in a gas by the methylene blue method. For best results samples should be tested within 2 hours after termination of gas scrubbing, and the sample should be cooled to 10° before amino acid reagent is added. The preferred absorbent for hydrogen sulfide in this method is 2% zinc acetate solution. When the gas sample contains 0.05 grain of sulfur as hydrogen sulfide, only 0.1 cubic foot of gas need be passed, and the result is obtained in less than 30 minutes. The proper wave length for use with the spectrophotometer is 745 mμ. As little as 0.00001 grain of sulfide sulfur per 50 ml. of solution can be detected by the methylene blue test. This amount of sulfur is equivalent to 0.001 grain per 100 cubic feet when the gas sample is 1 cubic foot.

Rapoport (*99*) reported that organic sulfur compounds can be individually absorbed by progressive absorptive liquids: 93% sulfuric acid for thiophene, 93% sulfuric acid and spindle oil for carbon bisulfide, while carbon oxysulfide remains behind. The organic sulfur contained in the gas after each absorption is determined by combustion.

Moisture. Pearson and Toye (*90*) determined moisture in producer gas. A small polarizing potential of 15 mv. is placed across tungsten-platinum electrodes dipping into the solution and the charges are amplified by a Mazda SP61 vacuum tube. The amplifier is coupled to a cathode-ray magic eye which serves as an indicator. A special titration assembly using two absorption vessels and titrator circuit are shown diagrammatically. Results given for the moisture content of a gas from an 11-foot Morgan producer are between 0.73 and 1.7 grams per cubic foot.

Zhdanova *et al.* (*129*) measured the moisture content of a gas using a 5% solution of cobalt chloride adsorbed on aluminum oxide or silica gel as a convenient indicator, after drying at 180° to 200°. The silica gel type changes color at 3 grams per cu. meter of moisture in air, while the aluminum oxide type changes at 1 gram per cu. meter; these correspond to dew points of −4° and −15°, respectively. Alternatively, the dew point determination can be used for determination of moisture. The gas flow is directed against a polished metallic mirror which is in contact with a thermocouple and is attached to a copper rod which can be cooled gradually by an external cold bath; this progressively lowers the mirror temperature. The dew point is determined by the clouding of the mirror and the moisture content is obtained from humidity tables.

Gallaway (*36*) used the infrared spectrometer to determine moisture in propane gas.

> The spectra of the wet and dry (or standard) samples are recorded between 5.8 and 6.3 microns with a wide slit on the spectrometer. The relative absorption in each spectrum is measured at the absorption maxima at approximately 5.89 and 6.05μ microns. The difference in the absorption at either point is obtained for the wet and dry samples. The moisture present is determined from a suitable calibration curve.

DENSITY

Nowlin (*87*) determined the specific gravity of natural gas for use in meter calibration by the orifice prover method from the ratio of the flow times of 5 cubic feet of dry air and natural gas (corrected for temperature, pressure, etc.) by using an orifice plate in series with a small positive pressure (diaphragm) type of meter. The same meter is also used for determining the "combined factor" (product of specific gravity factor times specific heat factor) by using a small orifice on the meter outlet. Detailed methods and precautions are given.

SAMPLING

McGlashen (*74*) describes equipment used for the safe collection from a high pressure source, of a representative sample of natural gas in a container having a safe working pressure considerably lower than that of the source pressure.

Förch (*31*) describes a method for obtaining a series of gas samples, each sample requiring no more than 2 seconds. Football bladders are connected by their intake valves to a series of T-shaped tubes connected by rubber tubing. The valve of each ball is provided with a string pinchcock. This apparatus is attached to the outlet valve of gas apparatus. When a series of samples is desired, the main valve is opened, and the pinchcocks are opened and closed at appropriate intervals.

Infrared and Mass Spectrometer Methods. Hunter, Stacy, and Hitchcock (*57*) used a mass spectrometer for analyzing mixtures of carbon dioxide, oxygen, and nitrogen. Response begins within 0.2 second and is complete after 0.1 second.

Neuert (*83*) gave a comprehensive treatise with many references on gas analysis with the mass spectrometer.

Shepherd (*112*) compares the results of analyses of a carbureted water gas by volumetric chemical methods and by a mass spectrometer in a series of frequency distribution plots. The spectrometric method gives a larger spread of values in the case of carbon dioxide, while the chemical method seems to give better reproducibility. The chemical method found considerable more oxygen than was present, and the mass spectrometer did not. Both methods yielded a wide spread of values in the case of nitrogen, with the chemical method plot seeming more to suggest the Gaussian pattern. Neither method seems to handle the determination of hydrogen too well. The chemical values are more closely grouped than are the spectrometric values in the case of carbon monoxide determinations; some of the laboratories used the combustion method and some the absorption method for the chemical determination and, as a consequence, two different peaks are present in the chemical plot. The mass spectrometer handles the determination of both methane and ethane much more effectively than does the chemical method. The two methods agree fairly well in ethylene determinations. A few of the spectrometric laboratories reported small amounts of other hydrocarbons present. Heating values calculated from the analyses indicate that the mass spectrometer probably gives greater accuracy, while the chemical methods give greater reproducibility. In the case of calculated specific gravity the chemical method appears to give the greater accuracy. The superiority of the mass spectrometer over volumetric methods seems to be limited to the hydrocarbon fraction of the sample gas and the spectrometric method needs considerable improvement in the determinations of hydrogen and carbon monoxide.

Shepherd (*113*) reports on the mass spectrometric analyses of a standard of carbureted water gas by laboratories cooperating with the American Society for Testing Materials. Reproducibility and accuracy of the mass spectrometer were shown by the data submitted by the cooperating laboratories in the various tables. The determination of hydrogen and of carbon monoxide with nitrogen was not altogether satisfactory. Several observations were made after comparing the data from the cooperative analyses. The differences between two calculators with the same spectrogram in the same laboratory were small. The differences between two operators with the same instrument in the same laboratory were small. The differences between spectrograms were larger than between operators and calculators.

Kambara (*62*) analyzed gas mixtures with a mass spectrograph (resolving power approximately 200). The concentrations of nitrogen, oxygen, and hydrogen in an air-hydrogen mixture were 53, 14, and 33%, respectively, while the calculated values were 51.0, 14.0, and 25.0, respectively.

Delsemme (*24*) used an infrared spectrometer to determine the trace components in gases by means of their absorption between 3 and 14 microns. A cell having a path of 1 ml. and containing 1 liter of gas was used.

TAR AND THE LIGHT OILS

TAR

Il'ina (*59*) perfected a method for the determination of carcinogenic substances, primarily 3,4-benzopyrene in tars. It consists in using paraffin oil as solvent for 3,4-benzopyrene and other carcinogenic substances. By this method 10^{-6} gram of 3,4-benzopyrene per gram of tar could be detected. When the content of benzopyrene was 10^{-5} gram, there was some indication of it in the spectrum, but a benzopyrene content of 5×10^{-5} gram per 1 gram of tar—i.e., 0.005%—was readily detected. By spectrographic analysis of the fluorescence spectrum with an apparatus of sufficient resolving power, the limit of benzopyrene determination can be extended considerably.

Vahrman (*123*) estimated the hydrocarbons in samples of primary coal tar chromatographically by using a steam-heated 6 × 0.5 inch column of silica gel. Before use, the silica was sized between 100 and 200 mesh and ignited at 500°. The tar (5 grams) was melted on the column and eluted with 100° to 120° petroleum ether until the eluant was colorless (3 to 4 hours). The eluant was evaporated on an oil bath under vacuum to constant weight. Eight determinations on one sample gave 52.5 to 54.4%.

BENZENE, TOLUENE, AND XYLENE

Landry (*69, 117*) determined benzene in the presence of its homologs.

> Samples for analysis are obtained by aspirating air at 0.25 liter per minute for 10 minutes through a U. S. Bureau of Mines bubbler for nitrating benzene. Toluene and xylene nitration products are selectively oxidized with chromium trioxide, and the dinitrobenzene is separated by differential solvency extraction with petroleum ether. The dinitrobenzene is taken up in a polarographic base containing 1 gram of metol, 31.5 grams of anhydrous sodium sulfite, and 6.3 grams of potassium carbonate in 250 ml. This solution can be polarized from 0 to 0.375 volt (*vs.* a mercury pool in the same polarographic base) to determine the dinitrobenzene wave height.

The wave steps obtained did not produce a straight curve when plotted against concentration, but the curve could be straightened out by plotting on log-log paper. The effect of the selective oxidation procedure is apparent, for treated dinitrotoluene has a very small step compared with the unoxidized nitrated compound. It is predicted that concentrations of toluene up to 1 mg. will not produce detectable wave steps in the procedure.

Vaughn and Stearn (*125*) developed a method of spectroscopic analysis of isomeric xylene mixtures. A working chart is illustrated wherein all possible proportions of the *o*-, *m*-, and *p*-isomers are represented in a triangular coordinate system enclosed within a graph representing the difference between optical densities at 2685 and 2625 A. as abscissas, and between 2725 and 2705 A. as ordinates. Reasons for selection of these wave lengths are given.

CRESOLS

Akita (*2*) worked out a satisfactory procedure for the quantitative analysis of *o*- and *p*-cresols by the cresoxyacetic acid method.

PHENOL

Martin (*76*) developed a rapid colorimetric method of estimating phenol. In a slightly ammoniacal solution and in the presence of potassium ferricyanide phenol reacts with 4-aminoantipyrene and gives a sensitive red color. The test is useful for determination of phenol in waters and brines.

Lambris and Haferkorn (*68*) described in detail a new method for the exact determination of phenols in low temperature tar and tar oils.

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FERROUS METALLURGY

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PRACTICAL advances in ferrous analytical chemistry embrace new reagents, new apparatus, and improved techniques. Methods for making analytical separations and for determining smaller amounts by simple procedures appear to be in growing demand.

Short (*143*) outlined methods for the determination of carbon, manganese, phosphorus, sulfur, silicon, copper, nickel, chromium, and aluminum in high purity iron (99.5+%). Malamand (*109*) described a spectrographic method for determining the chromium content of steel surface films of the order of 0.1 mm. thick. Ivanova (*85*) was able to analyze areas 0.1 mm. in diameter quantitatively with the spectrograph for manganese, chromium, nickel, and molybdenum in steel segregates by sparking through a perforation in a mica disk cemented to the steel. Gatterer (*61*) outlined methods of sample preparation, care of the spectrograph, precautions in the photographic process, and methods for interpreting results when using the spectrograph for determining traces of metals. Following these practices he was able to detect as little as 0.001% of halogens, sulfur, and selenium with a high vacuum discharge method of excitation (*62*). Wark (*159*) described a useful method for mounting semimicro samples for analysis by conventional arc and spark techniques. The use of inert atmospheres was found to enhance the emission spectra from the direct current arc (*152*) and a simple chamber for controlled atmosphere excitation was devised (*53, 127*). The effect of sample composition on the line intensity of different elements in the direct current arc was studied (*130, 140*).

Some exploratory work by Gorman, Jones, and Hipple (*69*) indicates that the mass spectrometer may, in time, be capable of use in determining all elements rapidly in steel. This technique remains in the developmental stage at present, however.

Holler (*81*) has compiled a useful bibliography on the sampling of ferrous and nonferrous alloys.

Pieters (*131*) presented a brief resume of methods for the analysis of pyrites.

Ductile zirconium was found by Petretic (*129*) to be a suitable material for crucibles used in sodium peroxide fusions.

Rules (*135*) compared the semimicro with the corresponding macro scale determinations from the standpoint of speed and accuracy, using representative volumetric, gravimetric, and electrolytic determinations. He found that semimicro scale values were obtained more rapidly and with equal accuracy to the macro results. Briscoe and Holt (*27*) published a useful reference on inorganic microanalysis.

Addink and de Groot (*2*) reviewed applications of the spectrograph which utilize direct current arc excitation. Bhaduri (*18*) used a rapid plate calibration method based on the relative intensities of the manganese lines at 2939 and 2933 A. for the quantitative analysis of high speed steels. Thiers (*149*) found that for step-sector speeds of greater than 40 flashes per second, the step-sector method is valid for film calibration. Shirley, Oldfield, and Kitchen (*142*) made a statistical study of spectrographic source units. Sukhenko (*145*) described a rapid method for the analysis of highly alloyed steels with the spectrograph. Riley (*134*) described spectrographic procedures that have been in successful routine use for analyzing cast iron. Carlsson and Yü (*41*) and Gillis and Eeckhout (*65*) utilized the spectrograph in analyzing slags.

Ahrens (*3*), Dingle (*51*), Harrison *et al.* (*78*), and Twyman (*151*) have written useful references on spectrographic methods. Other useful books have been on ultramicroanalysis (*96*), physical methods (*15*), colorimetric analysis for small amounts (*137*), and rapid test methods (*6*). A revised edition of "Methods for Chemical Analysis of Metals" was issued in 1951 (*5*), as was a useful list of AMERICAN CHEMICAL SOCIETY specifications for reagent chemicals (*167*).

ANALYTICAL SEPARATIONS

Accurate and simple methods for separating interfering elements are of growing importance in ferrous analysis. Such complex formers as sodium diethyldithiocarbamate, dimethylglyoxime, 8-quinolinol, nitrosonaphthol, cupferron, quinalizarin, and acetylacetone were investigated by immiscible solvent extraction of their metal salts to determine their value in analytical separations (*1, 103*) and for concentrating small amounts of different elements (*35, 67, 79*) prior to spectrographic analysis. The distribution of metal thiocyanates between water and diethyl ether was studied by Bock (*23*) for compounds of aluminum, beryllium, cobalt, gallium, indium, iron, molybdenum, tin, titanium, vanadium, and uranium. In some cases the normal thiocyanate, and in others the ammonium salt of the thiocyanic acid, was most soluble in the ether. Morrison (*117*) reviewed the analytical applications of extraction and the apparatus and techniques useful for such work. Sandell (*136*) reviewed the theoretical principles of separation by use of immiscible solvents. West (*164*) covered separation methods of recent origin that are useful in metallurgical analysis.

Chromatographic and adsorption techniques are of potential value in the separation of metals. Principles of chromatography have been outlined (*36, 105, 120, 171*). Ion exchange resins have been found useful for separation of iron from hydrochloric acid (*116*), from aluminum (*146*), and from titanium (*169*). The principles underlying their use were outlined by Schubert (*141*).

Magnetic stirring with a water-cooled bath was found greatly to facilitate separation of iron from such elements as aluminum with the mercury cathode and improved apparatus was designed to effect this separation (*42*). Facilities necessary for electrolytic separation were described by Ashley (*10*).

The use of thioacetamide (*56*) and thioformamide (*58*) in place of hydrogen sulfide for precipitation of such metals as arsenic and copper was shown to be feasible.

ALUMINUM

Use of organic reagents for the determination of aluminum appears to have received major emphasis during the year. Diethyldithiocarbamate (*45*), Stilbazo (*101*) [diammonium stilbene 4,4′-bis(1-azo-3,4-dihydroxybenzene)-2,2′-disulfonate], 1, 4-dihydroxy-5,8-dichloroanthraquinone (*100*), and 8-quinolinol (*90*) were investigated. Parker and Goddard (*128*) found that addition of the calcium ion enhances the sensitivity of the color reaction of aluminum with alizarin-3-sulfonate. Kassner and Ozier (*90*) utilized chloroform to extract aluminum 8-hydroxy quinolate from ammoniacal solutions (pH 8.9 ± 0.3) of iron containing tartrate, potassium cyanide, and hydrogen peroxide. The aluminum content of the extract was determined spectrophotometrically. Removal of part of the iron prior to extraction is necessary for steels low in aluminum.

Saxer and Jones (*139*) made a survey of methods of determining aluminum in iron and steel and described a useful modification of the phosphate method.

ARSENIC

Methods for determination of arsenic generally involve separation of the element from the iron matrix by distillation. Bertiaux

(*16*) investigated different distillation procedures and methods for estimating arsenic in the distillate. He considered the nephelometric procedure best for quantities of 0.008% and less and the permanganate titration better for large amounts. He considered the iodine and bromate procedures unsatisfactory. Belcher (*14*) recommended quinoline yellow as a superior indicator for the bromate titration. Kakita (*89*) recommended the iodine-thiosulfate titration for estimation of large amounts of arsenic in the distillate or the molybdenum blue reaction for small amounts.

BORON

Blumenthal (*22*) separated the boron from metal borides by precipitation of the metals with barium carbonate and sodium hydroxide, after bringing the borides into solution by fusion with sodium carbonate. The boron was then titrated potentiometrically in the presence of mannitol with 0.05 *N* sodium hydroxide. Kelly (*92*) separated the boron from steel as methyl borate and titrated the liberated boric acid in the presence of mannitol, using an 0.04% bromothymol blue solution as an indicator. There is a growing need for a simple, accurate method for determining boron in the range from 0.001 to 0.006% in an iron matrix.

CARBON

Efforts continue to be directed to the spectrographic determination of carbon in steel (*21*, *24*, *26*). These methods all utilize the 2296.86 A. carbon line. Blank and Sventitskiĭ (*21*) also used the 4267 A. line. They reported a mean probable error of 10%. Borsov (*24*) and his associates found that nickel, if present to the extent of 1%, interfered. Breckpot and Gobert (*26*) used an intense spark method of excitation, a medium dispersion spectrograph, and an electron multiplier tube for the carbon determination. A reproducibility of ±0.0008% carbon was obtained. Nickel interfered, but atmospheric carbon dioxide did not. Malamand (*110*) used the spark spectra excited between an aluminum wire and a flat steel specimen for determining carbon contents from 0.15 to 1.0% in mild steel. The mass spectrograph (*69*) also is potentially useful for the determination of carbon in steel.

Podkorytov (*133*) collected the products of combustion of steel at 1200° to 1350° C. in eudiometers graduated for up to 0.5% carbon in devising a method for determining small amounts of carbon in steel. Van Nieuwenberg (*153*) used a solution of barium hydroxide in a mixture of aniline, ethyl alcohol, and water for absorbing carbon dioxide. He obtained more efficient absorption with simpler apparatus. Wells (*162*) utilized a liquid oxygen trap for collecting the carbon dioxide liberated by combustion of the steel sample in devising an accurate method for small amounts of carbon in steel.

CERIUM

Utilization of cerium in steelmaking is responsible for an active interest in methods for its determination. Medalia and Byrne (*111*) devised a spectrophotometric method that utilizes the absorption maximum of quadrivalent cerium at 320 mμ; it is sensitive to 0.025 microgram of cerium. Excess persulfate or ammonium ion must be avoided. Miller and Kline (*113*) investigated the reaction of cerium in trace amounts with ion exchange resins and Wylie (*168*) explored separation of cerium from other elements as the nitrate by solvent extraction.

CHROMIUM

The behavior of chromium in contact with perchloric acid was investigated by Bertiaux (*17*) and associates. Brookshier and Freud (*34*) found that, at a pH of 1.7 ± 0.2 in the presence of 0.02 mole per liter of hydrogen peroxide, chromium could be separated quantitatively from vanadium and determined by means of its reaction with diphenylcarbazide. The method is said to be very sensitive and reliable for very small quantities. Gottlieb (*73*) and Murakami (*122*) also recommended diphenylcarbazide for the determination of small amounts of chromium. Butenko and Bekleshova (*39*) recommended the amperometric titration of chromium, manganese, and vanadium following oxidation with ammonium persulfate as superior to use of indicators. Pieters, Hanssen, and Guerts (*132*) preferred the spectrophotometric determination of these elements following oxidation with alkaline peroxide and potassium periodate. Kozlova and Korzh (*99*) were able to determine chromuim in ferrochrome with the spectrograph.

COBALT

A chromatographic method for isolating cobalt was investigated by Dean (*50*). He developed the cobalt complex of nitroso R salt and passed the specimen through an alumina column which adsorbed the cobalt complex and the excess reagent. Successive elution removed first the excess reagent and then the cobalt complex. The cobalt content of the complex then was determined spectrophotometrically. Katzin and coworkers (*55*, *64*, *91*) made an extensive study of the behavior of cobaltous compounds in different organic reagents. While not intended primarily for analytical use, this work should be valuable as a source of data for development of improved methods for determining cobalt. Lee and Diehl (*104*) investigated the reaction of 20 amines with cobalt. Benzidine was found to give a stable color with cobalt, which had an absorption maximum at 450 mμ. over a pH range of 4.8 to 7.0. West and de Vries (*163*) studied the cobalt-thiocyanate reaction. Kenny, Maton, and Spragg (*93*) separated iron from cobalt by extraction as the acetylacetonate with xylene at a pH in the range from 4.0 to 7.0.

COLUMBIUM

The effect of oxalate concentration and pH on the separation of columbium from tantalum by precipitation of the tannin complexes was studied by Bhattacharya (*19*). For complete separation of the tantalum complex from an 0.5 to 2.0% ammonium oxalate solution, the pH must be above 4.0. For complete precipitation of the columbium-tannin complex from the same solution, a pH of 4.6 is necessary. A single precipitation will make a complete separation if the tantalum pentoxide constitutes at least 75% of the total oxides. Goto and Kakita (*71*) were able to determine as little as 0.4 microgram of columbium per milliliter of solution by utilizing the yellow color produced with this element in the presence of pyrogallol and sodium sulfite in the pH range of 4.6 to 6.8. For tantalum, a solution 2 to 3 *N* in sulfuric acid was used to determine quantities as small as 50 micrograms per milliliter. Acetic, citric, succinic, phthalic, and the common inorganic acids did not interfere. Titanium, tungsten, and ferric iron interfered with the columbium precipitation.

Oka and Miyamato (*125*) described a method for determining columbium designed to avoid such difficulties as poor reducibility of Cb_2O_3 and hydrolysis. The specimen was fused in potassium acid sulfate, the melt dissolved in sulfuric acid containing hydrogen peroxide, and the solution reduced with a zinc amalgam. An excess of ferric sulfate and phosphoric acid are added and the ferrous iron is titrated with standard potassium permanganate. Young (*170*) found the spectrograph useful in determining the ratio of tantalum to columbium in the mixed oxides separated from steel.

COPPER

A solution of "cuproin" (2,2'-diquinolyl) in isoamyl alcohol has been found to be a specific reagent for cuprous copper (*66*). The complex is stable between pH 2 to 9 for approximately 72 hours with an absorption maximum at 546 mμ. Aluminum, iron, molybdenum, antimony, tin, titanium, and zinc interfere unless masked with tartaric acid (*82*). Copper has been determined amperometrically as the thiocyanate after reduction with hydroxylamine hydrochloride or sulfate (*106*). A weakly buffered acetic or tartaric acid solution was used. At concentrations from 0.01 to 0.001 *M*, the accuracy is said to be 1% with no interference from iron, manganese, chromium, nickel, or cobalt. Rubeanic acid (*114*) has been recommended for the colorimetric determination of copper in steel without separation from iron or common alloying elements. Nance (*123*) separated the α-benzoinoxime-copper complex from steel with chloroform and determined the copper spectrophotometrically. Webb (*160*) separated iron from copper as the hydroxide and reacted the copper with diethyldithiocarbamate for the spectrophotometric determination of copper in steel. Ovenson and Parker (*126*) made a spectrophotometric study of this complex. They extracted it with carbon tetrachloride from an aqueous solution 2 *N* in ammonium hydroxide and containing ammonium citrate. They found an absorption maximum at 436 mμ. The complex fades rapidly in light, but is stable for 1 hour in darkness. Manganese, bismuth, cobalt, and nickel interfere.

GASES AND NONMETALLIC COMPOUNDS

The spectrograph has been useful in analyzing segregates. Convey (*47*) reviewed methods for their identification and analysis without separation from the matrix. Veselovskaya and Koretskiĭ (*156*) were able to determine chromium with good accuracy in carbide residues extracted from steel by packing a mixture of the residue and copper powder in a hollow electrode and using a condensed spark method of excitation. The 2830.47 A. chromium and 2924.37 A. copper lines were used. The method for isolating the carbides was not described. Dymov and Gorelik (*52*) separated iron columbide from steel by anodic solution in 7% hydrochloric acid. Austenite and columbium carbide also were identified in the residue by x-ray diffraction methods. A better procedure was found to be solution in 10% cupric chloride solution in the presence of air followed by centrifuging to recover undissolved compounds. Aluminum oxide has been separated from magnet steels following solution with bromine dissolved in methanol (*33*). Lacomble (*102*) reviewed methods for isolation of nonmetallic compounds from steel. He described a method in which the steel is made anode in an electrolytic cell with a mercury cathode and an electrolyte composed of sodium chloride, potassium bromide, and sodium citrate. With a current of 20 to 25 amperes at 10 volts, approximately 20 grams of steel were dissolved in 45 minutes. Wada and Ishii (*158*) utilized a ferrous sulfate electrolyte containing citric acid for isolation of nonmetallic compounds. A current density of 1 A. per sq. dm. at 1 volt was used at room temperature. The pH of the electrolyte was held at 4. Low carbon and silicon steels and pig iron were examined. The residues were analyzed by conventional procedures.

Cook and Hobson (*48*) compared two methods of sampling and analysis for determining hydrogen in steel.

> By the "notched-pencil" method, liquid steel was removed from the furnace in a well-slagged spoon, skimmed, killed with a small amount of aluminum wire if necessary, and poured into a warmed special cast iron mold. The mold was immediately opened and the red hot notched-pencil quenched in water. The specimen nominally 0.5 inch in diameter by 0.5 inch long was descaled by light grinding, weighed, degreased, and placed in the vacuum heating furnace and held at 650° C. for 45 to 70 minutes (3 hours for austenitic steels). The extracted gases were then diffused through a heated palladium tube attached to the apparatus. If specimens were stored before analysis, they were held at −78° C. in solid carbon dioxide.
>
> The second method was the "sealed-mold" procedure, which differed from the notched-pencil method in that the killed metal was poured into a water-cooled mold, which was immediately sealed with a special cap and the mold and cap were immersed in water until both were cold. The gas within the mold was first collected and analyzed for hydrogen. Then the specimen was removed, prepared in the same way as the pencil specimen, and introduced into the extraction apparatus, where it was held for 1 hour at 750° C. The evolved gas was collected and analyzed for hydrogen with modified Orsat apparatus. Results obtained by the two methods were in satisfactory agreement.

Hurst and Riley (*84*) found that all hydrogen could be removed from steel by heating it in a vacuum for 1 to 2 hours at 600° to 800° C., but this treatment was not sufficient for iron. Torrisi and Kernahan (*150*) described a modification of the usual vacuum fusion furnace designed to make it less expensive to construct and maintain.

GERMANIUM

The color reaction of germanium with phenylfluorone (2,3,7-trihydroxy-9-phenyl-6-fluorone) was utilized by Cluley (*46*) for the determination of germanium following separation from interfering elements by distillation from hydrochloric acid. He also investigated separation as the sulfide and titration in the presence of mannitol. The color reaction of germanium with an oxidized solution of hematoxylin was made the basis for determining 0.08 to 1.6 p.p.m. (*124*). The germanium is separated by distillation and extracted from the distillate with carbon tetrachloride.

IRON

A series of articles by West (*165*) reviews the various methods for the determination of iron by colorimetric means. Wells (*161*) utilized a silver reductor and titration with 0.01 *N* sulfatoceric acid for determining 0.25- to 0.5-mg. quantities of iron. Sosnovskiĭ (*144*) determined metallic iron in ore by reacting the sample with 15 ml. of boiling 10% copper sulfate for 15 to 20 minutes, filtering, and titrating an aliquot (made acid with 7 *N* sulfuric acid) of the cooled filtrate with potassium permanganate.

MAGNESIUM

Following removal of iron by an ether separation, Cheburkova (*44*) removed copper with 8-quinolinol; then precipitated magnesium as the hydroxyquinolate and titrated it in acid solution with a 0.1 *N* bromide-bromate solution to a yellow color, using indigo carmine as indicator. Potassium iodide (0.5 gram) was added and the liberated iodine titrated with thiosulfate. Alternatively, after removal of iron, the magnesium may be precipitated as the ammonium phosphate. Hague and Schultz (*75*) removed manganese as the oxide following the ether separation and then precipitated the magnesium as the ammonium phosphate and ignited it to the pyrophosphate. Westwood and Presser (*166*) separated iron with isopropyl ether and removed other impurities with a sodium amalgam cathode prior to precipitating the magnesium in the usual way. Hugo (*83*) prepared a nitric acid solution of the sample and excited it in a special stand by means of a spark as the basis for a spectrographic method which gave an accuracy of 4 to 5% standard deviation. An alternative technique using the direct current arc and solutions baked in graphite electrodes is accurate to ±7% and is slower. Komarovskiĭ (*98*) excited the solid specimen by sparking between a copper electrode and the flat sample. The Mg 2807.7 and Fe 2806.97 A. and the Mg 2802.7 and Fe 2793.9 A. line pairs were compared. The method is said to be accurate within 0.001 to 0.003% in determining 0.02 to 0.14% magnesium. Argyle (*7*) used the 2802.7 magnesium and the 2799.3 A. iron line with spark excitation of solid specimens.

MANGANESE

A stoichiometric method for determining manganese in manganese ores, ferromanganese, Nichrome (*37*), ferrovanadium, and high vanadium steels (*38*) is based on the Volhard method with potentiometric titration using a platinum electrode in a neutral phosphate solution.

MOLYBDENUM

A solution of phenylhydrazine hydrochloride in 50% acetic acid solution is recommended for the spectrophotometric determination of molybdenum (*12*). Large amounts of ferric iron interfere. Haight (*76*) was able to determine molybdenum in the presence of the elements commonly present in steel by use of the polarograph and a perchloric acid electrolyte. Jungblut (*88*) utilized the thiocyanate complex in aqueous solution as the basis for a rapid colorimetric method.

NICKEL

The green color of nickel in perchloric acid solution was utilized by Bastian (*13*) with a technique of high precision for measuring absorption to determine the nickel content of high nickel (98 to 100%) materials. Nickel was determined by amperometric titration in an ammoniacal solution with dimethylglyoxime (*40*). Iron was complexed first with sodium fluoride. Cooper (*49*) worked out the details of a spectrophotometric method that gives good color stability and is reliable in the presence of copper and manganese. Ferguson and Banks (*54*) were able to detect smaller amounts of nickel with 1,2-cyclopentanedionedioxime than with dimethylglyoxime or 1,2-cyclohexanedionedioxime, but found that it had no advantage over these reagents with regard to the stability of the color produced. Gahler, Mitchell, and Mellon (*59*) were able to determine nickel after extracting the nickel complex of α-furildioxime at a pH of 8.1 with 1,2-dichlorobenzene by measuring the absorption at 438 mμ.

PHOSPHORUS

A micro modification of the familiar alkali-molybdate method for determining phosphorus was found by Mika (*112*) to be suitable for routine use. A 500-mg. sample was used and all reactions were carried out in a single vessel. The method is probably no faster than the usual procedure, but should be useful when only a small sample can be obtained. Kinnunen and Wennerstrand (*95*) formed a vanadomolybdate complex with phosphorus and extracted the aqueous solution with a mixture of 10 parts of ethyl alcohol and 1 part of butyl alcohol. The transmittance of the molybdivanadophosphoric compound was then measured. Sulfamic acid (*74*) was found effective in overcoming interference from nitrite in the molybdenum blue method for determining phosphorus. Hill (*80*) also described an improved molybdenum blue method. Hans (*77*) compared the Geiger tube with the electron multiplier for the spectroscopic determination of phosphorus. The ratio of the 2149 A. phosphorus to the 2497 A. iron line was used. Breckpot (*25*) compared results with the electron multiplier tube to those obtained photographically, using the ratios of the 2136.19 and 2149.11 A. phosphorus lines to the 2136.55 A. iron line. Results reproducible to within ±2% were obtained in 15 seconds.

SELENIUM

Selenium was determined in stainless steel by Mott (*119*), following solution in a nitric-hydrochloric acid (1 to 1) solution containing hydrofluoric acid. The solution was fumed with perchloric acid, cooled, and diluted to 250 ml. with hot water, 20 ml. of 25% aqueous hydroxylamine hydrochloride and 100 ml. of concentrated hydrochloric acid were added and the solution was digested on the water bath for 1 hour. The elemental selenium was then recovered in a Gooch crucible, dried at 105° C., weighed, and then ignited to expel the selenium. The loss in weight is equal to the selenium content.

SILICON

The yellow silicomolybdate complex was studied by Armand and Berthoux (*8*) for use in determining silicon. The complex develops rapidly and completely at pH 4.0 to 1.0 in the cold. The rate of formation decreases rapidly as the alkalinity increases above this range. This may be compensated for by increasing the temperature and the molybdate concentration.

Milton (*115*) recommended that the silicomolybdate be formed by boiling in a weakly acidic solution and the solution then made more acid (2 N is sufficient) before reducing the molybdenum. The corresponding compounds of arsenic and phosphorus will not reduce if the solution is more than 1.5 N in sulfuric acid. Care must be taken in dissolving the steel (*9*) to avoid high temperatures and long digestion periods which form high polymer silicic acids. Oxalic acid and ferrous sulfate have been found suitable for reducing the molybdenum (*31*) in low (0 to 0.05%) silicon ranges. Stannous chloride, which is unsatisfactory for the lower ranges, is good for a range from 0.05 to 2.0% (*28, 43*). Mohr's salt has been used in place of stannous chloride (*172*).

Gelatin has been found useful in recovering silicon by the gravimetric procedure (*87*). Goto and Kakita (*70*) dissolved steel in nitric acid, oxidized with potassium chlorate to eliminate carbon, and precipitated silicon from a 3 to 4 N nitric acid solution by addition of potassium chloride and 40% hydrofluoric acid. The precipitated K_2SiF_6 was dissolved in hot water and the silicon determined by titration with standard sodium hydroxide.

SLAGS AND REFRACTORIES

MacCardle and Scheffer (*108*) utilize the reaction of vanadium pentoxide in sulfuric acid with trivalent titanium for the determination of titanium in slags. The excess vanadium pentoxide was titrated with standard ferrous ammonium sulfate. Vignial and Andrieux (*157*) removed calcium carbide and free calcium oxide from slags with a 5% solution of sugar in ethylene glycol. Titration of the solution with standard potassium permanganate enabled the amount of each compound to be calculated. Sawaya (*138*) determined silicic acids in silicates following fusion with sodium carbonate by dissolving the melt in water, neutralizing with hydrochloric acid, adding an excess of potassium fluoride and a known excess of standard hydrochloric acid, and titrating the excess hydrochloric acid. The spectrograph also has been utilized for the analysis of slags (*41, 65*). A rotating electrode method has been found practical for the determination of aluminum, calcium, and iron in magnesite (*118*).

SULFUR

The evolution of sulfur from steel as hydrogen sulfide on treatment with dilute hydrochloric acid was found by Jaboulay (*86*) to depend on the composition of the steel and its thermal treatment. These facts were taken into account in the apparatus he designed for the sulfur determination. The usual iodometric method for estimating the hydrogen sulfide recovered from steel is not accurate enough for the most precise work, according to Kitchener and associates (*97*) who recommend alkaline sodium hypochlorite as a combined absorbing and oxidizing agent. The reagent was found to be stable to boiling and to give a quantitative oxidation of sulfide to sulfate. Goto and Morimura (*72*) burned steel samples in oxygen and absorbed the products of combustion in an alkaline peroxide solution; after adding ethyl alcohol and sodium rhodizonate as an indicator they titrated the sulfur dioxide and trioxide formed by oxidation of the sulfur, with an 0.02 N barium chloride solution.

THORIUM

High frequency titration was found by Blaedel and Malmstadt (*20*) to simplify greatly the volumetric determination of thorium. Analyses can be carried out more rapidly by their procedure, especially in the presence of certain impurities.

TIN

Following decomposition with mixed inorganic acids, tungsten is complexed with citric acid and the tin precipitated as sulfide in one procedure developed by the British Iron and Steel Research Association (*29*); in a second, the tungsten is separated by hydrolysis. Adsorption losses of tin are said to be low by either of the procedures, which were designed primarily for high tungsten material. In another procedure (*32*), tin is separated as the sulfide with molybdenum sulfide as a carrier. The isolated tin is reduced with aluminum and titrated with standard iodate. Kenyon and Ovenston (*94*) found the reaction of tin with dithiol to be a suitable basis for a spectrophotometric method.

TITANIUM

Peroxidized solutions of titanium were extracted into a 1% solution of 8-quinolinol in chloroform by Gardner (*60*) to enhance the color intensity of the titanium-peroxide complex. The extraction is not selective; small amounts of aluminum, iron, and molybdenum can be tolerated, but zirconium and vanadium must be absent. Two acceptable routine methods—a gravimetric based on use of cupferron and a colorimetric applied after oxidation to pertitanic acid—were published by the British Standards Institute (*30*).

TUNGSTEN

The variables in the stannous chloride–thiocyanate colorimetric method for traces of tungsten were studied with the object of improving the reliability of the method (*57*).

VANADIUM

The characteristics of divalent and trivalent vanadium in polarography were explored by Lingane and Meites (*107*). Murakami (*121*) separated iron and vanadium by successive extractions at different pH with a 2.5% solution of 8-quinolinol in 2 *N* acetic acid. The iron-free vanadium was reacted with sodium tungstate and the transmittancy measured at 434 $m\mu$. Telep and Boltz (*147*) found that in the absence of ferric iron and nitrate ions the absorption band of peroxyvanadic acid at 290 $m\mu$. can be utilized for the determination of vanadium. The common ferrous sulfate–persulfate titration method for determining vanadium in steel has been improved with a photometric device for determining the end point (*68*). A chromium to vanadium ratio of greater than 10 to 1 will produce high results. If tungsten is removed, other elements common in steel do not interfere.

ZIRCONIUM

The blue fluorescence of flavonol with zirconium in an iron-free solution was found to be a useful method for determining zirconium, especially for minerals containing less than 0.25% zirconium oxide. Iron can be removed with the mercury cathode. Gavioli and Traldi (*63*) found mandelic acid to be excellent for the gravimetric determination of zirconium in alloys containing from 0.36 to 3.65% of this element. Titanium did not interfere. This reagent was also found satisfactory for small amounts (*11*). From 20 to 25 minutes at 85° C. were found adequate for complete precipitation of from 0.01 to 0.025 gram. With smaller amounts a longer time before filtration was necessary.

Thamer and Voight (*148*) investigated chloranilate complexes of zirconium, some of which may have application in the spectrophotometric determination of zirconium. Fumaric acid (*154*) was found to precipitate zirconium from solutions up to 0.35 *N* in hydrochloric acid. The resulting gelatinous precipitate can be ignited to the oxide and weighed; a single precipitation was found sufficient for separation from aluminum, beryllium, nickel, barium, calcium, iron, manganese, and rare earths. In the presence of chromium, vanadium, tin, and titanium, a second precipitation is necessary. *m*-Cresoxyacetic acid was recommended as a specific reagent for zirconium (*155*).

SUMMARY

The literature cited in this review does not include all published articles; an effort has been made to include those describing specific methods and others of general value as reference material in an analytical laboratory dealing with a wide variety of ferrous materials. It is hoped that any important omissions will be brought to the attention of the editors, so that they may be included in a future article.

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NONFERROUS METALLURGY

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IN THIS review most of the references cover the period 1950–1951, although some are included from the latter part of 1949, in order to maintain continuity with the previous review of Churchill (*68*) published in 1950. At that time a trend toward increased use of instrumentation was indicated and this is still in evidence. There is considerable activity in the application and improvement of established chemical procedures, but somewhat less in the development of entirely new ones.

The variety of materials requiring analytical methods is rapidly expanding. Ores, metals, process solutions, coatings, finishes, slimes, slags, soils, atmosphere, and plant and animal tissues are only a few of the types of samples frequently encountered in nonferrous laboratories. Techniques of separation and measurement regarded as curiosities a few years ago are coming into everyday use. Based on publications appearing during the past year, the following observations may be made:

> Interest in the so-called "less familiar" elements has reached such proportions that they require serious consideration in the laboratory training of advanced students.
>
> Many high-purity metals are becoming important commercially and present new and interesting analytical problems.
>
> Even with rapid laboratory methods of analysis there is considerable demand for quick and decisive spot tests for use by nontechnical personnel in sorting metals.
>
> Use of instrumental inspection techniques is on the increase. Nonferrous analytical laboratories might well anticipate the demands for this type of service.
>
> The most important trend in the field of nonferrous metallurgical analysis at present is the transition from historical to control analysis through use of the direct-reading spectrograph. The full impact of this development is still to be felt, although the direct reader is firmly established in the aluminum industry, where it has had its widest application, and where it is already performing most of the metal analysis being done. Increased production, elimination of off-composition metal, and closer control yielding metal with maximum physical properties are the major contributions of the direct reader. Savings in manpower and laboratory space, although significant, are only incidental.

A large number of publications on analysis of nonferrous materials have appeared since the last review. Some are not referred to in this paper because the information is available in other sources or is not considered to be of immediate interest in a production laboratory. It is hoped that omission of significant contributions has been kept to a minimum; it is recognized, of course, that much information on some of the rarer elements such as uranium has not been published. For purposes of this review the discussion is organized according to the base metal concerned, except for the two concluding sections.

Several recent publications concerned with sampling are of general interest. A bibliography on the subject was compiled by Holler under the auspices of A.S.T.M. Committee E-3 (*147*). Chilled samples to avoid segregation were recommended by the British Standards Institute (*41*). Actual case histories of discrepancies in chemical analyses caused by segregation, inclusions, and other phenomena were reported by Niezoldi (*216*). St. Clair and Blue recommended use of a motor-driven agitator and cooling with a jet of water and compressed air to avoid segregation (*257*). Preparation of standard alloy samples for chemical analysis with detailed directions for melting, casting, and machining was discussed in a recent publication by the Istituto Sperimentali dei Metalli Leggeri (*152*).

ALUMINUM

New and enlarged editions of the standard sources on metal analysis, "Chemical Analysis of Aluminum" and "Modern Methods for the Analysis of Aluminum," have been published recently (*69*, *233*). Several papers on the polarographic determination of copper (*163*) as well as iron, lead, zinc (*262*, *290*), tin (*207*), and cadmium (*291*) indicate continued application of this instrument to metal analysis, particularly in laboratories not equipped with spectrographic facilities. Electrodeposition of copper from aluminum alloys and from brass and tin-base alloys in phosphoric acid medium without prior separations was proposed by Norwitz (*219*, *222*). Colorimetric methods for copper were described, one using diethyldithiocarbamate for 1 to 3% in the presence of nickel (*205*), and another designed for larger amounts employing the less sensitive reagent tetraethylenepentamine (*319*).

A colorimetric method for iron using 1,10-phenanthroline was described by Ryan and Botham (*255*). Maassen developed a rapid potentiometric titration method for manganese using ferricyanide and a back-titration with cobalt, suggesting also a method for cobalt (*185*).

An interesting vacuum furnace method for magnesium suitable for large-scale routine work was developed by Urech, Muller, and Sulzberger (*302*). A similar method was proposed by McCamley, Scott, and Smart for isolating sodium preparatory to a gravimetric determination (*186*). This is said to be the most sensitive of the published methods for sodium. A rapid method for sodium using a flame photometer was developed by Brewster and Clausen applicable over the range 0.0001 to 0.05% (*39*).

Phillips and Holton determined zinc with diphenylcarbazone (*240*), while Plank, Bodor, and Rády, interested in trace amounts, used the more sensitive dithizone (*241*). An indirect method by Biberschick was based on precipitation of zinc with diethylaniline and ferricyanide followed by photometric measurement of the precipitate (*25*). Cooper determined nickel with dimethylglyoxime (*73*) and Busev applied the thiourea method for bismuth to aluminum alloys (*50*).

In order to avoid losses in determining tin, Thery proposed alkali attack followed by separation of silica with perchloric acid (*298*). Tin was then determined photometrically or by electrodeposition. A useful qualitative test for tin using cacotheline was reported by Bourson (*32*).

Using the familiar ethylenediaminetetraacetic acid to mask aluminum interference, Meek and Banks determined beryllium colorimetrically with thiosalicylic acid in the near-ultraviolet (*195*). Brewster developed a promising method for determining boron with 1,1-dianthrimide (*38*). Like other boron methods, this employs a reaction in concentrated sulfuric acid, which is a disadvantage to some extent.

Some of the minor constituents of aluminum received attention, including sulfur (*184*), hydrogen (*78*, *296*), and oxide (*303*, *314*). Swain's method for hydrogen (*296*) in aluminum-magnesium alloy sheet is based on measurement of voids formed by immersion in molten potassium dichromate and can be correlated with the more elaborate vacuum-fusion method. Oxide is determined by the hydrogen chloride method (*300*) or with bromine in methanol; both methods leave something to be desired.

A new and simple acid attack method for soda in alumina is based on decomposition at 200° C. in a sealed tube with hydrochloric acid (*154*). This method should be of particular interest with calcined aluminas. Control methods for bauxite including chromium, phosphorus, zirconium, and sulfur were reported by Calzolari (*57*). Spectrographic methods for determining the principal constituents of bauxite using pelleted samples were described by Kler and Rezvova (*165*). For the analysis of sodium aluminate liquors, Watts and Utley developed methods for determining carbonate, hydroxide, and alumina on a single sample of aluminate solution (*312*).

Several papers of a general nature from foreign laboratories were concerned with spectrographic analysis of aluminum (*193*, *206*, *229*). Guiberteau described a recording instrument utilizing photomultiplier tubes which determines four constituents (*138*). Both arc (*97*) and spark (*251*) methods were reported for gallium in addition to a solution method for beryllium (*139*).

Methods of preparing and evaluating spectrographic standards were studied by Michel, who recommends chill casting on a cast iron plate to minimize segregation (*199*). Tikhomirova also discussed preparation of standards in rod form using a wheel-shaped chill mold (*299*). Oda studied sampling conditions spectrographically in addition to source conditions, particularly for silicon (*230*). Spectrographic analysis was used in studying aging effects (*183*) and diffusion in clad alloys (*43*). The problem of analyzing high-purity aluminum and other metals was studied by Smith (*279*) and by Bresky (*37*).

Considerable interest was shown in the rapid grading and identification of aluminum alloys spectroscopically (*294*) and by chemical spot tests (*180*, *213*). This is also true of other metals. Spot testing was the subject of a recent ASTM symposium.

Corrosion tests using hematoxylin, a very sensitive reagent for aluminum, can be carried out in 10 minutes and should be useful and practical (*11*). Morin was used for determining aluminum fluorometrically in corrosion tests on foil (*289*).

MAGNESIUM

Many laboratories analyzing aluminum are also interested in magnesium and, as a result, many publications on analytical methods are concerned with light alloys in general. Some of the references cited in the preceding section apply to magnesium as well as to aluminum—for example, the potentiometric titration of manganese (*185*) and a colorimetric method for zinc (*25*). A potentiometric method of titrating zinc in magnesium alloys with ferrocyanide was reported by Polyak and Shemyakin (*243*). As usual, the titration is performed at elevated temperature and smooth platinum and calomel electrodes are recommended.

A colorimetric method of Boettcher and Hellwig illustrates graphical methods of handling 2-component systems (*31*). They measured the colors developed by eriochrome cyanine and titan yellow without performing any separations and applied appropriate corrections by suitable calibration curves. Willard revived interest in dithio-oxamide (rubeanic acid) as a reagent for copper (*317*). This reagent offers advantages over some others in use particularly with iron present.

Spectrographic methods for aluminum, zinc, manganese, and silicon were studied by Puenzieux together with sampling methods (*246*). Smith described methods, equipment, and conditions for determining impurities in high-purity magnesium (*279*).

COPPER

The 1951 "A.S.T.M. Standards on Copper and Copper Alloys" contains much useful information on specifications for various nonferrous metals together with testing methods. This does not include the chemical procedures, however, which are to be found in "A.S.T.M. Methods for Chemical Analysis of Metals," along with methods for other nonferrous and ferrous materials.

For the determination of copper in sulfide ores, Goetz, Diehl, and Hach used perchloric acid to dissolve the sample followed by iodometric titration of the copper (*117*). With perchloric acid the ore dissolves in a few minutes, permitting a very rapid determination. McNulty, Center, and MacIntosh developed a procedure for selenium in pyritic materials and metallic copper, employing a distillation with hydrobromic acid and iodometric titration (*190*). For determining manganese and cobalt in slag, titration of manganese with permanganate and titration of cobalt with ferricyanide, both potentiometrically, were used (*116*). Young's detailed procedures for analysis of copper refinery slimes cover 20-odd elements plus the platinum metals and should prove to be very useful (*324*). Germanium and molybdenum in ores were determined spectrographically by arc and spark methods, respectively (*42*).

Two methods for aluminum in bronzes were reported, one gravimetric, using a mercury cathode separation (*204*), and a potentiometric titration method using sodium fluoride (*153*).

A thorough and authoritative discussion on the electrodeposition of copper was published by Skowronski and will probably stand as the most important source of information on the subject for some time (*276*). The determination of copper by the electrolytic method in copper-uranium alloys (*114*), silicon and aluminum bronzes (*122*), manganese bronze (*125*), silver solder (*127*), brasses and bronzes (*222*), silicon bronze hardeners (*227*), and tin bronzes (*245*) was also investigated.

Some of the papers cited include methods for the complete analysis of silicon bronze (*122*), manganese bronze (*125*), tin bronze (*245*), and beryllium-copper alloys (*17*). The polarograph was used for analyzing brass (*250*), copper-beryllium alloys (*176*), and other copper-base alloys (*270*). Seguin and Gramme reviewed the available chemical and spectrographic methods for analysis of beryllium-copper alloys (*260*).

Miscellaneous colorimetric methods were reported, including methods for manganese (*212*), nickel (*121*, *202*), iron (*124*, *221*, *228*) and aluminum (*59*, *269*) in bronze; nickel in Monel (*118*) and nickel silver (*120*); phosphorus, arsenic, and silicon in copper (*103*); and phosphorus in phosphor copper (*226*). An interesting method described by Jean for antimony in copper is based on a reaction with methyl violet, producing a blue product extractable with benzene (*155*). A rapid colorimetric method based on measurement of copper in hydrochloric acid was recommended by Goldberg and Dobbins for grading scrap nickel silver (*129*).

An improved method for determining traces of mercury in copper alloys was described by Miller and Wachter (*203*).

In order to avoid losses, they carefully dissolved the sample in sulfuric acid with added peroxide and reduced the mercury followed by distillation and titration with dithizone. The method is sensitive to 0.04 p.p.m.

Three papers on the determination of antimony in copper and alloys (*217*, *224*) were published, including a colorimetric method (*168*). Tin in manganese bronzes was determined by Norwitz, Boyd, and Bachtiger using a nitric acid separation (*225*). Interference by iron up to 1.3% was eliminated by boiling 30 minutes in nitric acid. Several publications on the determination of minor constituents included methods for silicide inclusions in manganese bronze (*325*); phosphorus in copper alloys gravimetrically (*159*) and by electrical conductivity (*309*); oxygen in copper, as well as in lead and tin, by hydrogen reduction (*12*); and sodium in tungsten bronzes (*191*).

Although microanalysis, the analysis of small samples, has not found very wide application in the metallurgical field, it should be of value for studying the composition of inclusions or other materials not available in large quantity. Miller and Currie (*200, 201*) demonstrated some of the possibilities of micromethods by determining lead gravimetrically in white metals, fusible alloys, and copper-base alloys using samples of 5 to 10 mg.

Micromethods of analyzing spectrographically some ancient bronzes were described by van Doorselaer (*84*). Samples of 4 mg. were used in order to consume as little of these samples as possible in view of their archeological interest.

Spectrographic methods of determining lead, zinc, nickel, and tin in bronzes were described by Gruszeck (*136*). Sampling of copper-base alloys for spectrographic analysis was investigated by Palmer, Irwin, and Fogg, who recommended pin-type electrodes prepared by remelting fine chips in a graphite crucible (*235*). The cast pins were then machined to the desired dimensions.

New possibilities of chromatographic methods were suggested by Srikantan and Krishnan, who determined copper in brass and bronze by adsorbing it on alumina and relating copper content to length of the chromatogram (*282*). Recoveries of 99% were reported. The same authors separated silver and copper chromatographically using zinc in dilute solutions, under which conditions it comes out between copper and silver (*283*). The usual order is Cu-Ag-Zn.

Interest in chemical spot tests for alloy identification remained at a high level for applications where spectroscopic facilities are not available. Nevers described tests for distinguishing coppers, high-copper alloys, bronzes, and brasses, with flow sheets for each group (*214*). Evans and Higgs described tests for fourteen elements in copper-base alloys suitable for use by nontechnical personnel (*94*). Kirtchik discussed the case where spot tests are required for distinguishing two or three known alloys and presented methods for such combinations as Monel and Inconel, various cobalt-nickel-chromium alloys, and some ferrous metals (*164*). Blanc recommended a silver nitrate test for aluminum in brasses and bronzes (*30*), and Nikitina discussed spot methods for bronzes and other alloys using filter paper as a reaction medium (*218*).

LEAD

During the period covered by this review, the number of publications concerned with analysis of lead alloys was exceeded only by those devoted to aluminum and copper-base alloys. For determining lead in ore materials containing barium, the chromate method was recommended, with an iodometric titration for small amounts and titration with Mohr's salt for larger amounts (*95*). Lead in babbitt alloys was determined by precipitation as the oxalate followed by titration with permanganate (*305*). Rázso (*248*) and Savelsberg (*259*) described methods for the complete analysis of bearing and type metals. Carrara determined zinc in type alloys titrimetrically by a thiocyanate method (*58*). A potentiometric titration method for thallium in lead-thallium alloys was used by Bertorelli and Tunesi (*23*).

According to recent work reported by Etheridge, separation of lead and bismuth in the analysis of fusible alloys is best accomplished by fuming with sulfuric acid as a temperature not exceeding 250° C. At higher temperatures, lead is invariably contaminated with bismuth (*93*). Methods for determining lead, tin, and antimony in lead alloys (*196*) including cable-sheathing alloys (*28*) were reported.

Methods for minor constituents included calcium (*34*, *35*) based on visual examination, selenium (*36*), oxide by hydrogen reduction (*12*), and nickel (*7*). Black's method for oxide was based on ammonia evolution (*28*).

In the polarographic analysis of tin-lead-antimony alloys, ethylenediaminetetraacetic acid was used to advantage in separating iron, copper, and bismuth waves (*99*). Rodewald developed a fairly satisfactory polarographic procedure for simultaneously determining copper, cadium, nickel, and zinc in bearing metals (*254*). For analysis of refined lead, the polarograph was used in determining tin and antimony (*173*) and, in addition to these, copper, cadmium, and zinc (*77*). Bismuth in pure leads was determined photometrically (*10*).

Several other colorimetric methods were reported applying to the determination of bismuth (*52*, *135*), copper (*123*, *268*, *320*, *322*), and arsenic (*274*). Manita studied conditions for determining lead in used solder employing a turbidimetric micro method (*192*). Bishop and Liebmann made quantitative separations of zinc from other metals by chromatography on cellulose columns (*27*). Activity in the field of chromatographic separations in metal analysis appears to be on the increase.

Dickens and Petit analyzed lead and tin alloys spectrographically using rotating electrodes prepared by casting the samples in the form of disks under molten potassium cyanide (*82*). Sensitivity is sometimes a problem in the spectrographic control of the purity of lead and this subject was considered in Smith's review of recent developments in lead analysis (*278*). Conditions for the spectrographic determination of antimony up to 16% in antimonial lead were reported (*149*) and methods for small quantities of bismuth in ternary lead-rich alloys were reviewed (*46*).

ZINC

The papers on analysis of zinc materials published since the last review (*68*) emphasize the growing importance of instrumentation, mainly polarography and spectrography. These two methods of analysis seem to be particularly useful in zinc analysis. Ores were assayed polarographically (*110*) and minor constituents including iron and lead were also determined (*263*). Interest in the germanium content of zinc materials was evidenced by two articles on the colorimetric determination of germanium in sphalerite (*88*) and in zinc refinery by-products (*215*).

Ford recommended the polarograph for rapid analysis of zinc-base, die-casting alloys in laboratories not having spectroscopic equipment (*105*). Copeland and Griffith developed an inexpensive manual polarograph for determining lead and cadmium in zinc, by which inexperienced personnel were able to analyze four samples per hour (*74*). Accuracy was comparable to that attainable by chemical and spectrographic methods.

As with various other nonferrous metals, interest in high-purity material was expressed and here again the polarograph found application in determining bismuth, copper, antimony, lead, tin, indium, and cadmium (*264*). The spectrograph was also used in analyzing high-purity zinc, although difficulties were reported by Bethune and Schmittroth, because of the small amounts of impurities to be determined and the low melting point of zinc (*24*). These authors recommended large cone-shaped electrodes (175 grams) which served to absorb the heat generated by their alternating current. Bresky described spectrographic procedures for analyzing high-purity zinc (*37*) and the general subject was also reviewed by Smith (*279*).

Woodruff described spectrographic methods for cadmium, iron, lead, tin, antimony, and aluminum (*321*). Using briquetted electrodes, he achieved accuracy surpassing that obtainable in some of the routine chemical determinations. Hans studied the use of photometric line width measurements and pointed out the advantage of being able to cover wide ranges of composition with a single exposure in the determination of lead, copper, tin, and cadmium (*141*).

Revised tentative methods for the chemical analysis of zinc powder for pigment were issued by the American Society for Testing Materials, Committee D-1, and include the determination of total zinc, metallic zinc, calcium, lead, lead, iron, cadmium, chloride, and sulfide (*4*). Oxide in zinc powder was shown to be extractable with ammonium acetate (*232*). Serfass and Perry described a colorimetric procedure for determining lead in zinc plating baths using dithizone (*265*).

Traces of lead in zinc were determined photometrically as the sulfide (*140*). Aluminum was determined photometrically in die-casting alloys with solochrome cyanine (*240*) and with eriochromecyanine R (*315*).

TIN

Using electrodeposition on a copper-plated cathode, Goldberg determined bismuth in alloys containing bismuth and tin with cadmium present (*128*). Yao and Yü employed the reduced molybdate colorimetric method for trace amounts of arsenic in tin (*323*). Their method offers considerable time saving compared with the conventional titrimetric method requiring a separation by distillation. Several publications were concerned with the analysis of tin plate and cover the determination of lead, copper, iron, antimony, and tin (*44, 209, 234, 258*). With Saito's electrolytic method, tin is determined from a current-time curve. Rapid methods for the analysis of babbitt included the colorimetric determination of iron (*126*) and tellurium (*130*).

CADMIUM

Little has been published recently on the analysis of cadmium materials. Two papers on the polarographic determination of zinc in cadmium were published by Kovalenko (*171, 172*). Cadmium was removed by electrodeposition on aluminum cathodes. For the determination of lead in high-purity cadmium metal, the polarographic method was recommended (*143*). Lead dioxide when deposited electrolytically from acid solution was found invariably to be contaminated with thallium, for which a satisfactory correction could not be applied. Thallium, however, is readily deposited from ammoniacal solution with good results.

BISMUTH

Delaney and Owen developed spectrographic methods for analyzing bismuth and lead-bismuth alloys using the porous cup technique (*79*). Detailed procedures for the following elements were described: beryllium, cobalt, chromium, iron, manganese, molybdenum, niobium, nickel, tantalum, titanium, vanadium, and tungsten. Polarographic analysis of bismuth and antimony alloys was investigated by Riccoboni and Zotta and their procedures apply to copper, bismuth, antimony, cadmium, and zinc (*252*). Funston and Reed developed a hydrogenation method for oxygen in bismuth (*106*).

NICKEL AND COBALT

As a result of difficulties in determining large amounts of nickel accurately by conventional methods, Bastian turned to the "differential" method using a spectrophotometer and was successful in analyzing alloys of 98 to 100% nickel with errors of only ±0.05% (*18*). The method was applied to electronic and spectrographic nickel, as well as to various synthetic mixtures, using the green color in perchloric acid measured at 720 mμ. This work suggests similar possibilities with other metals. Goldberg used colorimetric methods for determining nickel in Monel (*118*).

Small amounts of zinc in high-purity nickel were determined with dithizone after a preliminary separation with acridine and thiocyanate (*104*). Chepik recommended an electrometric titration with ferrocyanide for determining cobalt in cathodic nickel and nickel electrolyte (*63*). Phosphorus, arsenic, and silicon in nickel were determined by molybdate colorimetric methods using solvent extraction (*103*). To eliminate interference by other constituents, Potter recommended preliminary separation of silica followed by a carbonate fusion and measurement of the molybdenum blue color (*244*). Luke's photometric method for sulfur involving reduction of sulfate and measurement of lead sulfide is applicable to nickel as well as to numerous other metals (*184*). Spectrographic methods for determining small amounts of lead and antimony in nickel alloys using an alternating current arc were reported by Buyanov (*55*).

Lea developed a useful field test kit and procedures for rapid identification of certain nickel alloys such as Monel and Inconel as well as stainless steels (*177*). Chromatography with cellulose columns was employed by Burstall, Kember, and Wells for separating metallic impurities from nickel plating solutions (*47*).

For the colorimetric determination of aluminum in cobalt and other metals, Shemyakin and Barskaya suggested the use of Diamino Bright Blue FFG, a trisazo dye (*267*). Silverman and Lembersky developed an excellent gravimetric method for determining nickel in cobalt-base alloys using dimethylglyoxime, with cobalt in the 3-valent state oxidized by ferricyanide (*275*). Mevel described complete schemes for analysis of refractory alloys (*198*). Combustion methods for carbon were found to be unsatisfactory and a wet oxidation was recommended.

TITANIUM AND ZIRCONIUM

A symposium including discussion of the analysis of titanium was sponsored by the Armour Research Foundation of Illinois Institute of Technology in June 1951. Much useful information is available in the reports of this meeting (*188*).

MacCardle and Scheffer devised a method of determining titanium(III) in titaniferous slags based in oxidation with vanadium(V) and back-titration with Mohr's salt (*187*). Bischoff's method for titanium(IV), designed for various titanium-rich preparations, involves reduction with iron powder or wire in an atmosphere of carbon dioxide followed by titration with ferric sulfate (*26*).

For the spectrographic analysis of high-purity titanium, Peterson recommended use of the porous cup technique (*239*). Iron, manganese, and magnesium were determined in sulfuric acid medium. Corbett used the thiocyanate and periodate colorimetric methods for iron and manganese in titanium (*75*).

Because of their effects on the physical properties of titanium, dissolved gases, oxygen in particular, have been the subject of much analytical investigation and the end is not yet in sight. Walter described a vacuum-fusion method for oxygen and obtained excellent results, although the need for continued attention to this problem was pointed out (*311*). Derge also studied the oxygen determination and modified the procedure ordinarily applied to steels (*81*).

There is similar interest in the determination of oxygen in zirconium and several publications on the vacuum-fusion method as well as the hydrochloric acid–volatilization method have appeared recently (*249, 285*). Fassel and Anderson used a spectrographic method for analyzing mixed oxides of zirconium and hafnium, covering a wide range of concentrations (*98*). Samples were pelleted with powdered graphite and conditions were established permitting coverage of the entire range with one exposure by selection of suitable line pairs. Beaumont and Petretic described a colorimetric method for determining nickel in zirconium with dimethylglyoxime (*19*).

VANADIUM

Guenther and Gale used a molybdate colorimetric method for determining silicon in vanadium, separating the metal by extraction from acid solution with cupferron in chloroform (*137*). Their method is also applicable to uranium metal. A cupferron separation was also used prior to the determination of residual amounts of calcium in vanadium (*256*). Methods for the spectrographic analysis of vanadium ores and slags were reported by Buyanov (*54*). These include procedures for vanadium, calcium, aluminum, magnesium, iron, and silicon. Similar methods for chromium slags were also described.

BERYLLIUM

In a review on the analytical chemistry of beryllium, Furuhata discussed the separation of beryllium from aluminum and iron, colorimetric methods for beryllium, and a new color test for beryllium (*108*). Eberle and Petretic used Pontachrome Blue Black R for the fluorometric determination of aluminum in beryllium metal and oxide (*89*). Interfering constituents such as iron, titanium, and vanadium were extracted with cupferron in chloroform. Bane determined small amounts of lead in beryllium polarographically, using a method requiring no preliminary separations (*14*).

CHROMIUM

Furness investigated the determination of chromium in chromite and recommended the peroxide fusion method (*107*). By using nitroferroin indicator, interference by vanadium in the back-titration of excess Mohr's salt was avoided. Arsenate was found not to interfere. Oxide in chromium metal was determined by Short using hydrochloric acid attack following a vacuum annealing treatment at 800° C. Chromic oxide remains undissolved under the conditions used (*272*). Ogburn proposed a titrimetric method for chromium(III) in plating solutions based on precipitation as Na_2CrF_5 followed by oxidation with ammonium persulfate. Correction for occluded chromate was recommended (*231*).

MANGANESE

Several papers on the analysis of manganese ores and ferromanganese were published. Semenko discussed conditions for precipitation of manganese dioxide (*261*) and Jean studied the persulfate method for analysis of ferromanganese and minerals (*156*). Busev investigated the potentiometric titration of manganese(II) with permanganate and reported the reaction to be quantitative in neutral pyrophosphate solution (*49*). A platinum indicator electrode showed potential changes of 120 to 200 mv. at the end point. Chuiko used manganese sulfide as a collector in separating nickel prior to its colorimetric determination in manganese salts and ores (*67*).

MOLYBDENUM, TUNGSTEN, AND TANTALUM

Molybdenum and tungsten in ores were determined by Trnka using a carbonate fusion, precipitation with mercuric nitrate, ether extraction to effect separation fron chromate, reduction with mercury, and titration with ceric sulfate (*300*). Molybdenum and tungsten in alloys were determined by titration with chromous chloride following dissolution of the alloy in citric acid and hydrogen peroxide (*131*). Silicon in tungsten alloys was determined gravimetrically using phosphoric acid and aqua regia to dissolve the sample (*236*). For the determination of molybdenum and tungsten in tantalum-rich alloys, attack with nitric, hydrofluoric, and sulfuric acids was recommended followed by carbonate fusion of the residue (*210*). Lomonosova reported operating conditions for the spectrographic determination of titanium and niobium in powdered tantalum (*182*).

ALKALI METALS

Ellenburg, Owen, and Calkins applied the porous cup method, using platinum as internal standard, to the determination of the following elements in lithium: boron, beryllium, chromium, cobalt, iron, nickel, niobium, manganese, molybdenum, tantalum, titanium, vanadium, tungsten, and zirconium, all less than 0.1% (*90*). Sodium and potassium in lithium were run by Inman, Rogers, and Fournier using the flame photometer. Errors and corrections concerned with suppression and enhancement were discussed in their paper (*151*).

Pepkowitz and Judd published some interesting work on the determination of small amounts of oxide in sodium based on extraction of the sample with mercury to remove the metal (*237*). The undissolved fraction containing the oxide was then titrated or analyzed with flame photometer. Holt discussed the determination of hydrogen in sodium-potassium alloy by the vacuum-fusion method, indicating experimental difficulties and the need for improvements (*148*). A polarographic method for determining small amounts of chromium in calcium was described by Stage and Banks (*284*).

PLATINUM METALS, SILVER, AND GOLD

Spectroscopic methods have been very useful for analyzing alloys of the precious metals, particularly the platinum group. Platinum and palladium were determined spectrographically in some of the common sulfide ores (*145*). Recent papers were also devoted to the determination of trace impurities in platinum-rhodium alloys (*166*); palladium in platinum, platinum in palladium, and rhodium in iridium (*9*); and iridium and rhodium in intermediate products of platinum refining (*8*). Trace amounts of gold in silver were determined polarographically (*181*) and corrections were studied for silver errors involved in gold assaying (*253*).

URANIUM

Because of the limited amount of published information on the subject of uranium, any review of the literature is not likely to be up to date. A number of interesting publications have appeared, however, covering various phases of the subject from examination of minerals to the analysis of high-purity uranium metal. A handbook of chemical methods for determining uranium in minerals and ores includes a review of the available methods and gives recommended procedures in detail (*48*). A typical titrimetric method for uranium in ores involved dissolving of the sample in aqua regia, separation of iron by ether extraction, reduction of the uranium, and titration with dichromate (*170*).

Martens applied Murray and Ashley's colorimetric method for nickel to the analysis of uranium metal and oxides (*194*). Bane determined manganese colorimetrically by the periodate method (*15*) and molybdenum by the thiocyanate method (*13*). Haslam and Beeley determined up to 3% chromium by a perchloric acid oxidation method (*142*). Vanadium in uranium was the subject of a paper by Cowan who measured the vanadium as vanaditungstiphosphoric acid (*76*). As little as 7 p.p.m. may be determined by the proposed method, using a 5-gram sample. Walsh described spectrographic methods for the analysis of high-purity uranium metal covering the determination of iron, manganese, silicon, copper, and nickel (*310*).

NONDESTRUCTIVE TESTING

The American Society for Testing Materials has devoted considerable attention to the development of nondestructive tests for castings and wrought products. Although such tests are not usually performed in the analytical laboratory, they are of interest to those concerned with the supplementary analytical determinations often required. In a recent A.S.T.M. symposium on nondestructive testing, Van Horn reviewed the limitations and important applications of several widely used tests including radiographic, fluorescent-penetrant, magnetic-particle, and ultrasonic methods (*307*). McMaster and Wenk discussed features of nondestructive tests with reference to commercially available instruments (*189*) and the design and operation of several German instruments were described by Jellinghaus (*157*). The growing importance of ultrasonics is reflected in four recent papers (*72, 91, 100, 175*) and an A.S.T.M. symposium (*5*).

INDUSTRIAL HYGIENE

Analytical laboratories are contributing heavily toward the solution of problems involving industrial hygiene. Recent publications which will prove useful to nonferrous analysts dealt with the determination of numerous air-borne contaminants including chromium (*304*), lead (*6, 169*), thallium (*208, 273*), beryllium (*16, 238, 266*), and sulfur dioxide (*285*). Methods were described for various metals in sewage and industrial wastes covering the determination of cadmium, lead, zinc, chromium, copper, iron, manganese, and nickel (*53*).

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PETROLEUM

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ANALYTICAL CHEMISTRY continues to be an important factor contributing to progress in the field of petroleum. This is adequately illustrated in this review, which is concerned with the literature for approximately one year from that covered in the previous review (*60*).

CRUDE OIL

The Institute of Petroleum (*44*) studied the principles involved in the laboratory evaluation of crude oil. Morgan and Turner (*71*) concluded, from a study with iron, calcium, and sodium as radiochemical tracers, that if combustion is carefully controlled at ignition temperatures not exceeding 550° C., ash corresponding to quantitative recovery of metallic constituents of petroleum oil is obtained.

GAS

Podbielniak (*83*) reviewed the factors that influence the choice of methods and equipment for gas analysis by low temperature fractional distillation. Slobod (*101*) described apparatus for separating ethane from methane and air by refrigerating and pumping. LeRoy (*59*) modified the Boomer still to effect low temperature fractionation of very small samples of mixtures of hydrocarbon gases. Cremer and Muller (*13*) determined the composition of micro samples of gaseous mixtures by adsorption on charcoal or silica gel, using hydrogen to remove the unadsorbed gas and heat of conductivity for the determination; accuracy of approximately 1% was claimed and some mixtures were analyzed in 10 minutes. Koppius (*54*) described the application of a nondispersive double-beam infrared instrument for the analysis of hydrocarbon gases, employing hydrocarbons that occur in the mixture as filtering material in a special arrangement of cells to avoid interferences. Miller and Pearman (*69*) determined ethylene in mixtures free of other unsaturated materials, by shaking with an excess of an acetic acid solution of bromine; the excess was determined by titration with sodium thiosulfate after addition of potassium iodide. Marushkin and Belen'kaya (*67*) determined isobutylene in mixtures of other butylenes and butadiene by passing the gas into mercuric sulfate solution to produce the complex which is weighed, or dissolved in nitric acid, and its mercuric ion titrated with potassium thiocyanate.

Minter and Burdy (*70*) described a thermal conductivity bridge for analyzing ternary gas mixtures—for example, hydrogen and carbon dioxide in air—without the necessity of removing one of the constituents chemically, proposing the instrument for the analysis of any ternary mixture of gases whose constituents differ appreciably in thermal conductivity. Ruegg and Halpern (*94*), studying the efficiency of combustion processes, analyzed the exhaust gas by separating the water and carbon dioxide and burning the residual gas to determine combustible constituents.

Honig (*38*) employed the mass spectrometer to determine traces of impurities whose pattern is masked by the dominant constituents in the conventional application of the instrument. He employed ionizing energies in the ionization and appearance potential range. Reis *et al.* (*86*) reviewed the methods of analysis of hydrocarbon mixtures and described a mass spectrometer for which claims of superiority are made.

Harris and Nash (*30*) determined traces of water vapor in gas with a thermistor bridge to measure the rise in temperature when the gas was passed over calcium hydride; range of applicability was 0.001 to 0.1 volume % in hydrocarbon gases. Fluctuations in the composition of the gas do not affect the determination. Ilfeld (*42*) utilized an automatic dew point recorder for the determination of moisture in gases.

GASOLINE

Heigl *et al.* (*33*) described a Raman apparatus and method for determining olefins in liquid hydrocarbon mixtures, employing carbon tetrachloride—or a known blend similar to the unknown—to correct for changes in energy source and shifts in intensity; the result was computed from a relationship based on the area under the Raman curve. The scattering coefficients are proportional to the concentration of double bonds in the sample; the average coefficient for the olefins in each molecular weight range is a constant, though the values for the individual olefins in a particular molecular weight range may differ by as much as nine whole numbers. The olefin content is based on the Raman spectrum in the 1630 to 1680 wave number region. Dudenbostel (*16*) employed similar apparatus and method, but scanned the Raman spectrum at the 1590 to 1615 wave number region to determine aromatics in liquid hydrocarbon mixtures. The analyses of a number of synthetic blends had an average deviation of 5%. Woodward and George (*125*) pointed out that when a constituent is determined by Raman intensity, differences in the refractive index between a pure compound and the mixture may make it necessary to apply a correction particularly for hydrocarbon mixtures, such as paraffins and aromatics. Perry (*82*) described a rapid infrared method for analyzing mixtures of C_{10} aromatic hydrocarbons, involving one point base reference and logarithmic chart to simplify calculation of absorbances. Young *et al.* (*126*) determined type of substitution in aromatic compounds from the infrared patterns of benzene derivatives, in the 5- to 6-micron region.

Grosskopf (*24*) described an apparatus and method for microchemical chromometric determination of gases in air or other volatile substances, including benzene in vaporized motor fuel; the gas was drawn through a tube containing a solid carrier impregnated with indicator. Hadden and Perry (*25*) determined styrene in ethylbenzene by ultraviolet absorption at 2900 to 3100 A.; small amounts of benzene and toluene do not interfere. Marquardt and Luce (*66*) determined divinylbenzene in dehydrogenated diethylbenzene by precipitating its nitrosite and weighing; styrene interferes.

Leithe (*58*) determined normal paraffins in gasoline by treating with antimony pentachloride and dissolving the unaffected normal paraffins in carbon tetrachloride. Hibshman (*35*) used activated carbon to adsorb normal C_5, C_6, and C_7 paraffins selectively from iso-octane at room temperature. Landsberg and Kazanskiĭ (*56*) combined distillation and chromatography to separate aromatic hydrocarbons from straight-run gasoline and then dehydrogenated the remainder over platinum at 300° C. to convert the cyclohexane derivatives to aromatics. The specific hydrocarbons were then identified by Raman analysis of narrow distillation cuts. Brown (*9*) described a mass spectrometer method for analyzing gasoline for hydrocarbon types; cycloparaffins and mono-olefins are grouped and determined by chemical methods. Rock (*90*) discussed the features of mass spectra that are particularly useful for qualitative analysis of hydrocarbons, pointing out that one of the most valuable attributes of the mass spectrum of a mixture is that all constituents register and unexpected components do not escape detection. Purdy and Harris (*84*) described a constant-volume capillary pipet for introducing liquid samples into the mass spectrometer; the pipet is completely immersed in the pool of mercury of a sintered-glass valve to avoid introducing air with the sample.

Levine and Okamoto (*62*) discussed factors having a significant effect on accuracy of tetraethyllead determination by x-ray absorption, particularly when analyzing gasolines of different base stock and of different carbon to hydrogen ratio and density. Jirsa (*46*) reviewed the methods for qualitatively and quantitatively determining tetraethyllead in gasoline. He (*47*) also described a method for determining phenolic inhibitors in gasoline, based on extraction with alkali and treatment with Folin-Denis reagent.

KEROSENE AND HEAVIER FUELS

Adams and Richardson (*1*) investigated the utility of ultraviolet absorption spectra for identifying aromatic hydrocarbons in Diesel fuel, presented the spectra of many consecutive fractions, and provided information on the azeotropic displacement of boiling points of aromatics. Spakowski *et al.* (*107*) described a procedure involving chromatography, specific dispersion, and sulfonation for analyzing wide boiling petroleum mixtures. Robinzon and Yakshev (*89*) determined naphthene content of kerosene by combining sulfonation with measurement of physical properties, claiming agreement with the more tedious catalytic dehydrogenation procedure. Eckart (*17*) described an approximate method for determining naphthalene in tar oil, involving distillation with oil as carrier; the visible naphthalene crystals in the distillate were collected and weighed and correction was made for their solubility in the oil.

LUBRICATING OIL

Waterman (*121*) described the development of a method, based on refractive index, density and molecular weight, for determining percentage of carbon in aromatic rings, naphthenic rings, and paraffinic chains and for determining the average number of aromatic rings, naphthenic rings, and total rings per molecule. Hersh *et al.* (*34*) presented an excellent review of methods for determining average number of rings per molecule, average weight per cent of rings, and average weight per cent of carbon in the ring, and described a simplified procedure involving merely refractive index and molecular weight after prior separation into aromatic and nonaromatic portions by silica gel adsorption. Charts for obtaining molecular weight from refractive index and boiling point are illustrated and a recommendation is made that petroleum fractions be first simplified by distillation, adsorption, extraction, etc. Wanless *et al.* (*120*) described methods for characterizing high boiling petroleum products containing polynuclear aromatic hydrocarbons, involving refractometry, chromatography, ultraviolet absorption, selective extraction of some aromatic hydrocarbons with aqueous caffeine solution, maleic anhydride adduct formation, and oxidation. Varsanyi (*117*) determined alkylaromatic constituents by ultraviolet absorption, showing that this property of the homologs changes gradually so that the curve of a single homolog can be used. O'Neal and Wier (*76*) described a heated sample introduction system for the mass spectrometer, which permits liquid volume measurement and complete vaporization of hydrocarbons up to C_{40}.

Pagliassotti and Porsche (*78*) used a rotating graphite disk as lower electrode dipping into the sample to deliver it to the analytical gap in determining metals in oil by emission spectroscopy. Snyder and Clark (*106*) determined phenolic additives in lubricating oil with *n*-amyl alcohol solution of phosphomolybdic acid to produce the molybdenum blue complex, which is then extracted with an ammoniacal solution of ethylene glycol–amyl alcohol and determined colorimetrically.

Sinyakova *et al.* (*100*), studying the wear of bearings, combined chemical and polarographic procedures to determine iron, lead, copper, and tin. Wilson and Garner (*124*), studying corrosion by lubricating oil, determined peroxides by adding sodium iodide and a mixture of chloroform and glacial acetic acid, refluxing, and titrating with thiosulfate to a starch end point. Kolthoff and Medalia (*53*) concluded from a study of peroxide procedures, that iodometric methods are more accurate than ferrous iron methods; the latter are capable of gross errors, particularly when oxygen is not excluded.

ASPHALT

O'Donnell (*75*) described a method for determining hydrocarbon types in asphalt, involving molecular distillation, silica gel adsorption, dewaxing, urea adduct formation, and thermal diffusion; he thereby determined paraffins, naphthenes, aromatics, resins, and asphaltenes. Vahrman (*116*) employed adsorption on heated silica gel columns to determine hydrocarbons in tar, employing naphtha to elute the hydrocarbons.

SPECIALTIES

Seidman (*96*) employed infrared absorption to determine decahydronaphthalenes in a mixture of the isomers with noninterfering components. Lee *et al.* (*57*) studied the iodine monochloride method for determining unsaturation, pointing out errors resulting from decomposition of the reaction product followed by further reaction of the iodine monochloride with the decomposition product. They described a new procedure in which the addition of the reagent to the olefin or polymer is faster than its addition to the decomposition products; this results in greater accuracy for branched olefins and polymers. Newell (*74*) employed ultraviolet absorption at three wave lengths to determine styrene in polystyrene and to recognize the presence of interfering substances. Goldspiel and Bernstein (*23*) applied x-ray diffraction for the identification of crystalline substances in natural and synthetic rubber. Hofer and Peebles (*37*) used x-ray diffraction to identify crystalline aromatic hydrocarbons using iron target radiation, with little interference from impurities.

Zahner and Swann (*128*) determined phenol in cresylic acids by percolating a cyclohexane solution of the mixture through a column of specially wetted silicic acid, following changes in the percolate by ultraviolet absorption. Knapp *et al.* (*52*) employed infrared spectrophotometry at 13.37 and 12.92 microns to determine *o*- and *m*-cresols in *p*-cresol. Kelley (*50*) extended the utility of the mass spectrometer for the analysis of oxygenated compounds by heating the inlet tube, and suggested that for plant control purposes similarity of process samples with control mixtures should often provide sufficient information without the necessity for detailed component analysis. Kreshkov and Bork (*55*) described a qualitative test for organic silicon compounds, involving sodium carbonate–sodium peroxide fusion on a platinum loop; they completed the detection colorimetrically by addition of ammonium molybdate and benzidine acetate to the water solution.

POLLUTION

Cadle *et al.* (*10*) studied condensation methods for collecting and concentrating atmospheric contaminants for analysis and found increased collection efficiency when using a metal packing in the liquid nitrogen traps. Turkeltaub (*114*) determined traces of methane and ethane in air by adsorption on special activated carbon, from which the hydrocarbons are successively elutriated quantitatively. Stitt *et al.* (*109*) determined traces of ethylene in air by passage over red mercuric oxide at 285° C. and then over selenium-sensitized paper at 125° C. The mercury vapor, resulting from oxidation of ethylene, reacts with the selenium to discolor the test paper and the length of discoloration is the basis for the determination. Brinker and Williams (*7*) determined traces of carbon monoxide in air by scrubbing to eliminate all except carbon monoxide, oxygen, nitrogen, and hydrogen and then comparing the hydrogen ion concentration of this residue before and after combustion. Mader *et al.* (*63*) determined sulfuric acid in air by filtering through specially washed filter paper; they completed the determination by electrometric titration, claiming over 90% recovery. Snijders (*105*) determined small amounts of hydrogen sulfide in air by aspirating through bismuth chloride and measuring the discoloration of the solution. Moses and Brumbaugh (*72*) described improvements in apparatus for automatically recording hydrogen sulfide concentration by measuring light absorption of lead acetate–impregnated tape.

ELEMENTS

Boos and Conn (*5*) determined phosphorus microchemically in organic compounds by sodium carbonate fusion followed by amperometric titration with uranyl acetate. Amperometric titration with dichromate at a rotating platinum electrode was employed by Parks and Lykken (*80*) to determine copper and iron in residues obtained from used lubricating oils. These same authors (*81*) employed amperometric titration, or semimicro gravimetric precipitation, to determine silver in new and used lubricating oils which may contain many other elements. Telep and Boltz (*110*) utilized ultraviolet spectrophotometry to determine vanadium as peroxyvanadic acid at 290 and 460 mμ. Cassidy (*11*), in studying engine wear, used the emission spectrograph to determine elements in the ash of Diesel lubricating oil.

Agazzi *et al.* (*2*) described a miniature oxygen bomb which they used to determine chlorine and sulfur in 5 to 150 mg. of organic samples, the former by titration, the latter microgravimetrically. Mansfield *et al.* (*64*) determined halogens and sulfur in engine deposits by diluting with zinc and silver powders to form pellets and analyzing with the emission spectrograph, using a stream of helium through the analytical gap to minimize background and increase detectability. Thinius (*111*) employed tetrahydrofurfuryl alcohol solution of potassium hydroxide to determine chlorine in aliphatic polymers. Desassis and Macheboeuf (*14*) determined bromine in organic materials by reduction with metallic sodium, then reaction with gold chloride and photometric measurement of the orange-yellow color that develops. To determine fluorine in solid hydrocarbons which also contain chlorine, bromine, and nitrogen, Rickard *et al.* (*87*) decomposed the sample at 1100° C. in a stream of moist oxygen and determined the fluorine colorimetrically with ferric ion–salicylic acid reagent, obtaining similar results in quartz, platinized quartz, or platinum combustion tubes. Clark (*12*) determined fluorine in organic compounds by combustion with oxygen at 900° C. in a quartz tube with platinum catalyst; the combustion products were absorbed in water and the fluorine was determined volumetrically.

Harris *et al.* (*29*) determined oxygen in organic materials by modifying the Unterzaucher procedure to recirculate the pyrolysis products, in a closed system over carbon at 1100° C., until conversion to carbon monoxide is complete; hydrogen is eliminated during the circulation by diffusion through heated palladium. The carbon monoxide content of the resulting gas is determined by thermal conductivity. Large samples can be handled; hence the method is applicable to samples of very low oxygen content. Brown and Hoffpauir (*8*) employed pyrolysis with calcium oxide to detect nitrogen in organic compounds, using 8-quinolinol–zinc complex as fluorescent indicator. Kirsten and Olausson (*51*) described an ultramicronitrometer for determining minute amounts of combined nitrogen in mineral oil by the micro-Dumas procedure. Thompson and Morrison (*112*) determined small amounts of combined nitrogen in organic compounds by Kjeldahl digestion and nesslerization, without distilling the ammonia out of the reaction mass. Frederickson and Smith (*20*) determined nitrogen in organic compounds with the emission spectrograph, by maintaining an inert atmosphere (carbon dioxide) in the arc chamber, so that the cyanogen spectrum results from nitrogen in the sample and not from nitrogen in air.

SULFUR AND ITS COMPOUNDS

A small oxygen bomb for burning a few milligrams of sample for sulfur determination was described by Siegfriedt *et al.* (*98*); the bomb washings are titrated with barium chloride using tetrahydroxyquinone as indicator. Using the same reagents, Walter (*119*) employed a photometric method for recognizing the end point. Levine and Okamoto (*61*) as well as Hughes and Wilczewski (*40*) described methods for determining sulfur in petroleum products by x-ray absorption and discussed the effects of density, C-H ratio, and nature of base stock. Barthel *et al.* (*4*) determined sulfur in solid fuels by burning in an oxygen bomb and titrating the resulting sulfate with barium acetate conductometrically. Fischer and Sprague (*19*) also employed conductometric titration to determine sulfate, but employed benzidine dihydrochloride as titrant. Roth (*92*) determined traces of sulfur in organic materials by oxidizing to sulfate, reducing the latter by hydriodic-formic acid mixture to hydrogen sulfide, which is used to form methylene blue, and this is determined photometrically. Sands *et al.* (*95*) used a turbidimetric method to determine barium sulfate equivalent to the organic sulfur in synthesis gas. Tighe *et al.* (*113*) employed an infrared lamp to avoid deposition of sample on the wick when determining sulfur in naphthalene by the lamp combustion method.

Kalichevsky (*48*) reviewed methods for detection of free sulfur in petroleum products. Gerber and Shusharina (*21*) described a polarographic procedure for determining free sulfur and disulfide. Zurcher and Luder (*129*) determined corrosive sulfur in oil by reacting with silver at 110° C., reducing the silver sulfide to hydrogen sulfide in a stream of hydrogen, and completing the determination iodometrically. Matthews and Parsons (*68*) determined corrosive sulfur in oil by reacting with copper strip, which is then reduced electrolytically; cupric sulfide, cuprous sulfide, and cuprous oxide are distinguishable by plotting the potential across the electrodes as a function of time. Uhrig and Levin (*115*) determined free sulfur in gasoline by treatment with mercury, comparing the discoloration with standards.

Sneddon (*104*) discussed an instrument (Titrilog) for automatically and continuously titrating hydrogen sulfide and mercaptans with bromine which is electrolytically generated; the end point is determined potentiometrically. Mapstone and Davis (*65*) employed alcoholic silver nitrate to detect polysulfides in gasoline, interfering mercaptans being eliminated by prior treatment with aqueous silver nitrate solution. Wainwright and Lambert (*118*) determined thiophene in synthesis gas by reacting with isatin after eliminating hydrogen sulfide and mercaptans, completing the determination spectrophotometrically. Hartough (*31*) determined color reactions of related thiophene compounds with hexanitratoammonium cerate and proposed a new color test for organic sulfides. Armstrong *et al.* (*3*) employed infrared absorption at 9.48 microns to determine thionaphthene in naphthalene. Rapoport (*85*) determined carbon disulfide, thiophene, and carbonyl sulfide in gas by successive loss in sulfur content after passage through 93% sulfuric acid for thiophene, 93% sulfuric acid and spindle oil for carbon disulfide; carbonyl sulfide is unabsorbed. Hale *et al.* (*27*) studying the distribution of sulfur compound types in petroleum and the effect of temperature, concluded that heat, as in distillation processes, may change the concentration and types of sulfur compounds sufficiently to affect the analytical results.

CATALYSTS

Harmon and Russell (*28*) described an alternating current spark spectrographic method for determining iron, vanadium, nickel, and sodium in cracking catalysts. Osthaus (*77*) described improvements in the chemical determination of sodium and potassium in clays. Hunt *et al.* (*41*) applied the infrared spectrophotometer to analysis of minerals by grinding them to a powder, which is subsequently deposited as a film on a rock salt window.

Spectra, over the range of 2 to 16 microns, are shown for many minerals. Hale and Hale (*26*), studying the burning rates of carbon deposited on cracking catalysts, devised a method to follow the progress of combustion, based on changes in conductivity of a solution of sodium hydroxide used to absorb the carbon dioxide formed on burning. Ivey (*45*) studied methods for determining particle size of cracking catalysts and the factors influencing them. He proposed a modification of the Roller method involving specially humidified air to eliminate static electricity.

Kamack (*49*) described a centrifugal pipet sedimentation method for particle size determination of dusts and industrial powders in the range of 0.1 to 2 microns. Ergun (*18*) showed that density changes with particle size, the smaller particles having greater density. He described a gas flow method for determining particle density. Innes (*43*) determined surface area by continuous adsorption measurement under conditions where amount of gas adsorbed is proportional to time, the surface area is computed from time to reach a predetermined pressure end point.

MISCELLANEOUS

Smith *et al.* (*102*) reviewed the development and standardization in the American Society for Testing Materials of a U-shaped bicapillary pycnometer, comparing its precision on isopentane and gasoline with the Bingham pycnometer and specific gravity balance. Glasgow *et al.* (*22*) described a method and apparatus for determining freezing point at saturation pressure of hydrocarbons and organic sulfur compounds. Spear and Herrington (*108*) described a high temperature viscometer of the rolling sphere type suitable for temperatures to over 300° C. Its translucent glass precision-bore tube is contained in a metal block which serves as the constant temperature bath; no bath liquid is employed. Hoeppel (*36*) described an instrument for determining viscosity and gel strength of thixotropic fluids, such as drilling muds. A rotational viscometer, in which current to the electric driven motor is related to viscosity, was described by Boyle (*6*). Rouse *et al.* (*93*) discussed the factors affecting viscosity measurement with a torsion crystal, observing, incidentally, a shear elastic effect in measurements on certain additive oils.

Smith *et al.* (*103*) employed mercury vapor as heating medium in a still, to obtain flash vaporization data and by changing the pressure in the mercury boiler, varied operating temperature from 400° to 800° F. An automatic receiver changer for vacuum distillation, involving an intermittent siphon to deliver the distillate, was described by Simpson and Sutherland (*99*). Donnell and Kennedy (*15*) studied operating characteristics of concentric tube fractionating columns of high separating efficiencies. Rose, *et al.* (*91*) reported the results of an investigation on the effect of holdup to charge ratio on sharpness of separation of binary mixtures.

Young (*127*) determined the cloud point temperatures of dark Diesel oil by determining its viscosity as the oil cooled. At the cloud point a precipitation or separation occurs, resulting in abnormal viscosity behavior. Hotten and Kibler (*39*) described miniature penetrometer cones for determining consistency of grease. The construction and geometry of the cones result in a rectilinear relationship with penetrations obtained with the ASTM cone.

Narsimhan and Saletore (*73*) determined the neutralization number of oils by titration with aqueous alkali, avoiding the tendency of the resulting soap to hydrolyze by emulsifying the sample. Shaefer and Balling (*97*) employed a diethylene glycol solution of potassium hydroxide to determine saponification number of difficultly saponifiable esters, excluding the effect of atmospheric oxygen by adding phenetole to the reagent. Parks and Lykken (*79*) reviewed methods for microdetermination of constituents of petroleum products, involving potentiometric, amperometric, and polarographic methods. West and Hale (*122*) reviewed polarographic methods employed in the petroleum industry for the determination of metals, sulfur compounds, oxygen, naphthalene, and acetaldehyde. A mass spectrometer for monitoring continuous industrial processes, was described by Robinson *et al.* (*88*). Harvalik (*32*) employed infrared radiation to identify colorless substances absorbed in a chromatographic column, by converting the radiation to visible light with an electronic image convertor. Wiberley (*123*) described improvements in the Karl Fischer titration to enable less skilled operators to determine water in petroleum products.

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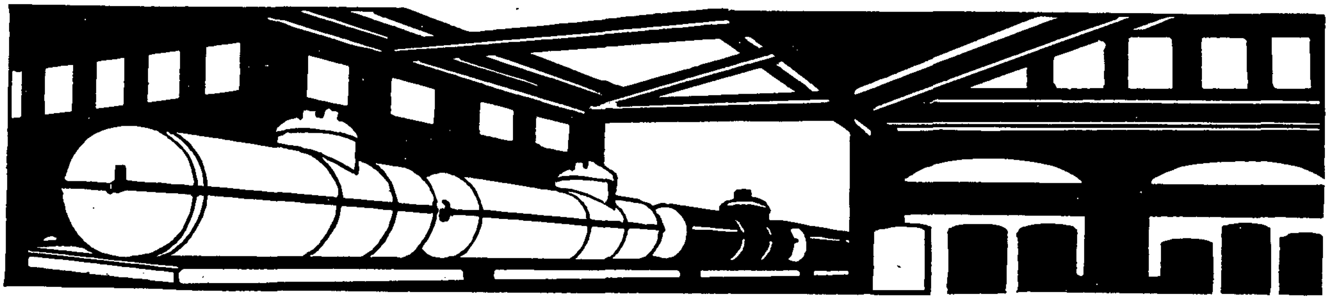

Pharmaceuticals and Natural Drugs

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AS IS the case in all the major fields of the science, the literature pertaining to analytical chemistry is rapidly approaching a state of practical unwieldiness. One might say—and not too facetiously—that a detailed search of published information for an analytical project in applied analysis could conceivably involve a large proportion of the time devoted to the project itself. The number of annual published contributions to analytical studies of pharmaceutical and natural drugs alone is estimated to be nearly a thousand.

The preparation of a review covering such a number and diversity of publications necessarily poses several problems. Foremost among these is the matter of selection of material, since it is obvious that an abstract of the contents of each article could not be included. The authors wish to repeat and to re-emphasize the fact that omissions from the review do not imply that the papers so omitted do not contain useful information. A conscious effort has been made, however, to include those studies and procedures which offer the greatest possibilities for use in pharmaceutical analysis.

The classification of methods is the same as that published in the previous annual reviews of pharmaceuticals and natural drugs.

CHEMICAL METHODS

ALKALOIDS AND RELATED SUBSTANCES

The physical and chemical characteristics of the alkaloid neprotine have been described and the structural formula has been suggested (*39*). A separation procedure involving paper chromatographic techniques for some of the cinchona alkaloids has been described by Lussman, Kirch, and Webster. The solvent system was cyclohexanol or cyclohexanone–hydrochloric acid. Alkaloidal zones were identified by their fluorescence or by color reactions (*125*). The estimation of aminophylline by potentiometric titration has been found to produce results which compare favorably with the U.S.P. method (*10*). Some modifications of the U.S.P. aminophylline method as applied to theophylline have been found to increase the precision of results. The modifications of the argentometric method consist of cooling the mixture before filtration and of omission of ammonia (*85*).

The lack of specificity of some color tests for cardiotonic heterosides (*20*) has been pointed out by Bellet. Paper chromatographic separation procedures for certain cardiotonic glycosides have been described recently (*102*, *139*, *179*). Compound zones were identified by various color or fluorescence reactions.

ANTIBIOTICS

Chemical methods which have appeared in recent months for the separation and determination of penicillin include a procedure involving the precipitation of procaine from solutions of procaine penicillin with subsequent iodometric determination of the antibiotic (*198*). Partition chromatography of the tertiary amine salts of the mixed penicillins has been accomplished on a silica gel column using water and tertiary amine as stationary phase and an organic solvent as the mobile phase (*122*).

Volumetric methods for the determination of streptomycin and dihydrostreptomycin have been reported by Delaby and Stephan (*48*). These authors described a qualitative test for streptomycin in dihydrostreptomycin utilizing Nessler's reagent. The test is capable of detecting as little as 2% streptomycin. An interesting report by von Euler and Heller indicates that streptomycin precipitates nucleic acid specifically. Neither polysaccharides nor nucleosides are precipitated by it (*60*). A preliminary note describes certain color reactions of aureomycin, chloramphenicol, and terramycin with Carr-Price reagent, phosphotungstic acid, ferricyanide, and other reagents (*151*).

CHEMOTHERAPEUTIC AGENTS

The titration of certain organic compounds including antipyrine, oleic acid, and resorcinol has been accomplished in nonaqueous medium utilizing lead acetate, mercuric acetate, bromine, and iodine monochloride as titrants. The medium involved was glacial acetic acid (*185*). Hald (*89*, *90*) has described a method for the determination of small amounts of 4-chloroacetanilide in phenacetin. Thiouracil and its alkyl derivatives have been titrated conductometrically with standard sodium hydroxide solution (*4*). A modification of the National Formulary method for the determination of resorcinol in ointments has resulted in a more satisfactory extraction procedure for this material (*194*).

HORMONES AND RELATED SUBSTANCES

Certain corticosteroids having a common characteristic in an alpha-beta unsaturated 3-ketone group have been shown to react quite specifically with osmium tetroxide (*132*). This observation suggests that the reaction may be of value in detecting steroids in extracts of biologic fluids. The separation of some corticosteroids and related substances on paper strips has been reported (*33*). The solvent systems used were toluene–propylene glycol and formamide-benzene. Complex formation between cortisone and iodine has been investigated by Bassil and Boscott (*12*). Cholic acid and androst-4-en-17α-ol-3,11-dione-17-carboxylic acid interfere by forming a blue color also. Saturated sodium bicarbonate containing iodine bleaches these complexes but not the cortisone complex.

A gravimetric method for the determination of progesterone in corn oil or sesame oil solutions can be applied without preliminary extraction (*41*); the steroid is precipitated by 2,4-dinitrophenylhydrazine. Several paper chromatographic separations of steroids have appeared recently. These include the utilization of alumina-impregnated filter paper (*34*) for the separation of progesterone, estrone, and estradiol. Zinc chloride in absolute alcohol (*152*) has been shown to produce characteristic colors and fluorescent products when sprayed on paper chromatograms of steroids as a means of identifying individual steroid zones. Another separation technique involving paper impregnation utilizes Quilon (stearato chromic chloride) as the stationary phase and simple primary alcohols as the mobile phases (*117*). A still different paper chromatographic procedure concerns a "reversed phase" system wherein the paper is rendered hydrophobic with silicone (Dow-Corning No. 1107). In this case the nonpolar phase is stationary while the polar phase (ethyl alcohol–water) is mobile (*118*). McMahon, Davis, and Kalnitsky (*130*) described methods for the paper chromatographic separation and identification of several nonketo steroids.

METALLIC IONS AND RELATED SUBSTANCES

The formation of a slightly soluble barium borotartrate complex has permitted the microdetermination of the borate anion (*74*). As little as 5 micrograms of boron at a concentration of 1×10^5 can be detected.

The Schwarzenbach method for the determination of calcium by titration with disodium ethylenediamine tetraacetic acid has been applied to certain pharmaceutical products (*86*). The titration utilizes Eriochrome Black-T as the indicator. A small amount of magnesium ion added to the solution permits greater precision in visual end-point determination. A similar technique has found application in the determination of hardness in water (*88*). An improvement in the Nitroso R salt method for the determination of cobalt which makes use of the adsorbability of the cobalt complex on alumina has been developed. The complex may be eluted with sulfuric acid. Interferences from copper, chromium, nickel, and iron are eliminated (*46*). The separation of mercury from interfering materials has been accomplished by distillation as mercury metal from acid solution (*140*). Up to 15 micrograms of mercury can be distilled in this manner and titrated in the distillate with dithizone. Another method for the determination of mercury involves complexation of mercuric ion by acetone with the formation of two hydrogen ions; thus, mercuric ion may be determined alkalimetrically. Iodide, bromide, cyanide, and thiocyanate ions interfere (*63*).

In the determination of nitrogen by the Kjeldahl procedure, solutions of nickel ammonium sulfate have been found to be suitable absorbents (*23*). Wingo, Davis, and Anderson have observed that if the boric acid–containing distillate in the Kjeldahl procedure is boiled to sharpen the end point or if water is drained from the condenser at the end of distillation in order to steam-out the condensers, low results are obtained. These authors indicate that solutions of ammonium borate when boiled will lose some ammonia (*202*).

An improved method for the volumetric determination of sulfate ion requires the addition of an excess of standard barium chloride to the solution. Excess barium ion and a small known amount of magnesium ion are added and titrated with standard disodium dihydrogen ethylenediamine tetraacetate using Eriochrome Black-T indicator. Reasonable results are obtained with concentrations as low as 5 parts per million (*148*).

PROTEINS AND AMINO ACIDS

The R_f values for the paper chromatographic separation of 34 lower peptides have been reported by Knight (*111*). Certain proteins and amino acids have been shown to have characteristic time reaction curves when titrated oxidimetrically with potassium cupri-3-periodate. These curves permit certain deductions concerning constitution (*16*, *17*).

Chromatographic procedures for the separation of amino acids continue to receive considerable attention in connection with the characterization of protein hydrolyzates and for the analysis of amino acid mixtures. Ion exchange resins (*156*, *157*) have been studied with respect to the displacement technique, while powdered cellulose columns have exhibited the advantage of separating protein hydrolyzates into neutral, basic, and acidic fractions (*22*). The results of the detailed examination of the effect of the pH of the sample are reported by Landua *et al.* on the paper chromatographic separation of these acids (*121*). By utilizing filter paper buffered to a selected pH, McFarren (*128*) has developed a one-dimensional separation scheme for 20 common amino acids.

VITAMINS

It has been found that saturated sodium chloride solution is a satisfactory stabilizer for ascorbic acid during the course of its extraction from certain natural materials (*135*). A precautionary factor to be noted with respect to oxalic acid extractions containing ascorbic acid is the rapid loss of the vitamin when it is exposed to sunlight. Special precautions were found to be necessary to protect these extracts during assay (*120*). With regard to interferences in the determination of ascorbic acid, it has been found possible to separate reductone (enoltartronaldehyde) by means of paper chromatography with the system butanol–acetic acid–water (*195*).

Paper chromatography has also found further usefulness in the separation and determination of small quantities of nicotinamide and nicotinic acid (*99*, *112*, *205*). The cyanogen bromide reaction was used to detect the presence of these materials on the paper strips. Pantothenic acid has also been separated chromatographically on acetate-buffered alumina columns (*45*).

Extensive investigations concerning the structure and properties of vitamin B_{12} have resulted in the disclosure by Brink, Kuehl, and Folkers (*30*) that vitamin B_{12} contains a cyano group bound coordinatively to the cobalt atom. Vitamin B_{12a} does not contain this group. Similar conclusions have been arrived at independently by Veer *et al.* (*190*). The photolysis of vitamin B_{12} on exposure to visible light with the formation of vitamin B_{12b} has also been observed by these authors. The conversion of vitamins B_{12a} and B_{12b} to vitamin B_{12} (cyanocobalamin) by addition of cyanide ions has been observed (*105*, *197*). The formation of a purple blue color in vitamin B_{12} solutions containing excess potassium cyanide has likewise been reported (*176*, *197*, *204*).

Separation procedures for irradiation products of ergosterol make use of the paper chromatographic technique (*130*).

GENERAL

The detection of acrolein from the enzymatic or thermal decomposition of glycerol in medicinal oils has been accomplished by reacting any acrolein present with aromatic primary amines to give a red color (*167*). Certain aldehydes and ketones have been separated on an anion exchange column in the bisulfite cycle. The substances are retained on the column and can be eluted by washing with sodium bicarbonate or sodium carbonate solution (*70*).

It has been noted by Domange and Pinguet that the U.S.P. test for the detection of nitrobenzene is not specific (*50*). Coupling color reactions for aniline are more specific. Jacobs (*100*) has published a rapid acidimetric determination of alum in alum-precipitated biologicals. The technique involves sequestration of aluminum with potassium fluoride, liberating 3 moles of potassium hydroxide for each mole of aluminum. The liberated alkali can then be titrated. With some exceptions, amines more strongly basic than pyridine form ether-insoluble salts with β-resorcylic acid, while those weaker than pyridine do not. Most aromatic amines do not form salts with this reagent (*201*). The free amines are regenerated by shaking with alkali.

A new fluorescent reaction of keto bile acids involving treatment with potassium ferricyanide and butanol has been reported (*143*). The fluorescence is readily perceptible in solutions containing 20 parts per million of dehydrocholic acid. The scope of utilization of potassium cupri-3-periodate as an oxidimetric titrant has been discussed by Beck (*15*, *18*). Several titrations of organic compounds such as glycerol, formaldehyde, acetic acid, resorcinol, and inositol are described. A comprehensive study of the oxidation of ferrous iron by organic hydroperoxides is reported by Kolthoff and Medalia (*114*). A simple relative method for the determination of peroxides utilizing ferrous ion has been developed. Potassium hydroxide dissolved in a mixture of ethylene glycol methyl ether and xylene is considered to be an ideal reagent in a simple and rapid method for the determination of saponification numbers (*87*). Gailey (*71*) detected the presence of ethyl vanillin in vanilla extract by means of paper chromatography. The solvent system used was butanol-ammonia and the spot reagent was 2,4-dinitrophenylhydrazine. An acidimetric method for the determination of vanillin involves alkaline peroxide oxidation to form 5 equivalents of acid per mole (*172*). The titration of inorganic anions in organic media offers many possible useful techniques for material of pharmaceutical interest. Markunas and Riddick (*133*) report the potentiometric titration of several salts of strong bases and weak acids or of weak bases and weak acids with perchloric acid in a glacial acetic acid medium. Other methods also using glacial acetic acid as a medium and perchloric acid as a titrant are those for the determination of phosphate, halide, nitrate, and nitrite ions (*94*) and of alkali halides and amine hydrochlorides (*95*). The latter methods involve visual titration with methyl violet or other indicators.

Of the common inorganic anions only sulfate and bisulfate cannot be titrated as bases according to this method.

Other nonaqueous titration methods involve the estimation of weakly acidic substances, such as organic acid imides, salts of amines, and phenols dissolved in basic solvents (butylamine) or benzene-methanol. The titrant is sodium methoxide in methanol. Indicators may be thymol blue or an antimony-glass electrode pair (*69*).

A peroxide test method for determining the stability of oils and fats is reported by Golden (*76*). This accelerated test is conducted at 125° C. with ferrous thiocyanate reagent as the testing medium. The procedure reports a 75 to 90% saving in time over the Swift stability test.

PHYSICOCHEMICAL METHODS

ALKALOIDS AND RELATED SUBSTANCES

The potentiometric titration curves for a number of alkaloid salts in aqueous alcoholic solvents have been determined (*168*). When alcoholic solvents are used there is sufficient inflection in the titration curves to allow accurate quantitative assay of the salts. Propanol in the mixed solvent gives the sharpest end point of the titration. As in the separation of other materials having similar characteristics paper chromatography has again been utilized to advantage in the separation of certain alkaloids. Some alkaloids of the ergot group and the strongly basic solanaceous alkaloids have yielded to chromatographic separation techniques involving buffered filter paper (*35*). The use of aqueous ammonia as the mobile phase in the paper chromatographic separation of a mixture of scopolamine, atropine, apoatropine, and belladonnine was investigated (*169*). In this particular separation the type of paper is important. Whatman, Barchman-Green, and Schleicher-Schüll papers produced no separation between scopolamine and atropine. The separations of similar alkaloidal groups using propanol-water and acetone-water systems are reported by Munier and Macheboeuf (*149*).

It has been noted that a smoother reaction of *p*-dimethylaminobenzaldehyde with the lysergic acid moiety of the ergot alkaloids proceeds in the presence of manganous ions (*144*). A fluorophotometric method for the determination of papaverine which is based on the conversion of the alkaloid to fluorescent coralynsulfoacetate can accurately estimate as little as 100 micrograms of papaverine. However, other interfering opium alkaloids, such as narcotine, must be separated before the determination can be made (*193*). Colorimetric methods for atropine, hyoscyamine, scopolamine, and homatropine consist of forming the addition products with bromocresol purple, extracting into benzene or chloroform, decomposing in alkali, and measuring the dye photometrically (*53*). Jindra and Pohorsky (*103*) recently published details of their ion exchange methods for the isolation and determination of alkaloids in natural materials. Amberlite resin IR4B (sodium carbonate regenerated) is used as the exchange column from which the free alkaloids are eluted with alcohol. The conversion of colchicine to colchiceine by acid hydrolysis and subsequent reaction of this product with ferric chloride is the basis for a colorimetric method for the estimation of this alkaloid (*109*). Lobeline may also be determined colorimetrically by first hydrolyzing to form acetophenone. The acetophenone is then distilled off and reacted with 2,4-dinitrophenylhydrazine to form the phenylhydrazone, which may be extracted into carbon tetrachloride and finally measured by determining the amount of light absorbed (*136*).

A rapid colorimetric method for the assay of xylocaine involves precipitation of the reineckate, dissolving the precipitate in acetone, and measuring the light absorption of the resulting solution (*153*).

The antihistaminic drug neohetramine has been found to contain the structural specificity required to produce color with 2-thiobarbituric acid. A method based on this reaction has been described recently (*62*).

A scheme for the fractionation and fluorometric estimation of digitalis glycosides has been compared with the cat and pigeon lethal equivalent procedures (*170*). Small quantities of gitoxoside in the presence of digitoxoside are detected by means of a reaction with phosphoric acid (*161*); by adding hydrazine hydrate to the phosphoric acid a yellow discoloration which interferes with the reaction is prevented and a quantitative method with a sensitivity of 1 microgram for gitoxoside is obtained.

ANTIBIOTICS

An isotope dilution method for the determination of penicillin G in broth samples involves the use of C^{13}-labeled penicillin G (*44*). The isotopically labeled crystalline penicillin G is added to the broth and a sample of penicillin is then isolated. The percentage of C^{13}-labeled material in the isolated sample is then determined with a mass spectrometer. Based on the fact that the relatively stable hydroxamic acid derivatives of the various penicillins show different partition coefficients between isopropyl ether–isopropyl alcohol and phthalate buffer, Baker, Dobson, and Martin (*8*) have developed a paper chromatographic procedure for the qualitative and quantitative measurement of the various penicillins.

Streptomycin and mannosidostreptomycin have been separated from interferences in fermentation broths by means of exchange on Amberlite IRC-50 resin (*166*). The antibiotics are released from the resin with dilute sulfuric acid. The colorimetric maltol and anthrone methods are used to determine the amounts of streptomycin and mannosidostreptomycin, respectively, the results by the maltol procedure being corrected for the amount of mannosidostreptomycin shown to be present. The amperometric microtitration of streptomycin and dihydrostreptomycin has been reported by Conn and Norman (*42*). The titration involves the formation of insoluble salts with anionic dyes. When heated in 0.25 *N* sulfuric acid for 2 hours, dihydrostreptomycin shows a well-defined absorption peak at 265 mμ (*97*). The spectrophotometric measurement of this product is the basis for an ultraviolet absorption method for the determination of dihydrostreptomycin; comparison with bio-assay on 24 commercial samples showed a range of 91 to 109% (per cent of bio-assay).

Two colorimetric methods and one spectrophotometric method for the assay of terramycin have been published (*145*), together with their range of application and comparison with microbiological assays. Qualitative tests for identification of terramycin are also given.

CHEMOTHERAPEUTIC AGENTS

Para-aminosalicylic acid has been determined by estimation of the color developed on coupling with *p*-dimethylaminobenzaldehyde (*173*). A rather specific procedure for the estimation of antabuse (tetraethylthiuram disulfide) involves the reduction of this substance with cuprous iodide with the resultant formation of the cupric diethyldithiocarbamate complex. A solution of the complex in carbon tetrachloride may be examined photometrically (*51*). Dulcin may be determined photometrically after reaction with silver nitrate, followed by treatment with manganese dioxide. The color formed is extracted into isobutyl alcohol prior to measurement of its absorption (*73*). The spectrophotometric determination of cineole (eucalyptol) is accomplished after reaction in anhydrous methanol with *p*-dimethylaminobenzaldehyde (*134*). Histamine in biological materials has been estimated after purification by reaction with 2,4-dinitrofluorobenzene (*129*). After purification of this derivative the solution may be assayed spectrophotometrically; as little as 0.5 microgram of histamine can be determined with good accuracy.

Of considerable interest with regard to the analysis of phenyl mercuric or ethyl mercuric compounds is the fact that these materials form complexes with dithizone which are soluble in chloroform; prior digestion of these compounds is not necessary. Inorganic mercuric ions do not interfere in this determination (*141*).

It is reported that thiouracil and methylthiouracil in pH 8 borate buffer, react with an ethanol solution of 2,6-dichloroquinonechloroimide to give a yellow product soluble in chloroform (*126*). Accurate determination of as little as 10 micrograms of thiouracil is claimed.

HORMONES AND RELATED SUBSTANCES

Descending paper chromatograms in the system butanol-acetic acid produce satisfactory separation of adrenaline and noradrenaline. Zones on the strip are cut out—position is judged from a guide strip sprayed with potassium ferricyanide solution—and extracted with dilute acid. The extracts may be then treated with sodium cyanide, ammonia, and arsenophosphotungstic acid to develop a photometrically measurable color (*101*).

Fluorometric methods for the determination of natural estrogens include a reaction with phthalic anhydride (*72*) and sulfuric acid (*13*). The fluorescence spectra of nine naturally occurring estrogens were determined with interference filters (*14*). A modification of the Zimmerman reaction in which 3,5-dinitrobenzoic acid was used in place of *m*-dinitrobenzene has been reported as the basis of a quantitative colorimetric method for certain keto steroids (*184*).

METALLIC IONS AND RELATED SUBSTANCES

Willard and Dean reported a polarographic method for the determination of aluminum (*199*). The procedure is based on the reduction of the complex of aluminum with Pontachrome Violet SW. The total diffusion current remains the same as for the dye alone but a portion of the curve proportional to the aluminum concentration is displaced approximately −0.2 volts from the half-wave potential for the dye itself. An unsuccessful attempt to use the silver–silver chloride electrode pair for the potentiometric determination of chloride in biological fluids is discussed by Duxbury (*54*). It is shown that this electrode pair may be used for the rapid and accurate determination of chloride in simple nonbiological fluids.

The application of paper chromatographic techniques to the separation and determination of potassium is the subject of an article by Beerstecher (*19*). Potassium is separated from interfering substances on a paper strip using the solvent system ethyl alcohol–0.1 *N* hydrochloric acid. The spot developing agent is $NaPbCo(NO_2)_6$. Planimetry of the spot serves to estimate the potassium concentration; by statistical analysis of several sample results, potassium can be determined with an error of less than 10%. Bassett and Byerley (*11*) report the determination of potassium colorimetrically by precipitating potassium silver cobaltinitrite, dissolving the precipitate in sodium hydroxide, diazotizing the nitrite, and coupling with 1-naphthylamine sulfanilic acid. The resulting color is measured photometrically.

The use of benzidine dihydrochloride for sulfate determinations has been investigated (*65, 66*). Results indicate that incomplete precipitation in the presence of foreign ions is probably due to imperfect crystal formation and growth. These authors describe a conductometric titration method involving solution of the sample in 30% aqueous ethanol at pH 3 to 7; phosphate ion interferes. A simple potentiometric method for the determination of sulfate involves titration of the sample containing added methanol and ammonium persulfate with standard barium chloride solution (*182*). Suitable electrode pairs for this titration are tungsten-calomel, tungsten-molybdenum, or platinum-tungsten.

PROTEINS AND AMINO ACIDS

A spectrophotometric micro method for the determination of methionine is based on a reversible reaction with iodine (*7*). Protein hydrolyzates may be treated directly. Methionine-containing peptides do not interfere. In the reaction of tryptophan with *p*-dimethylaminobenzaldehyde, elimination of interferences by chloride and bisulfite may be accomplished by treating the amino acid solution with silver sulfate. The precipitate is centrifuged and the supernatant liquid may than be analyzed (*177*). The mechanism of the reaction between certain aldehydes and the tryptophan nucleus has been investigated by Giral and Laguna (*75*).

VITAMINS

A detailed comparison of most of the known methods for the estimation of ascorbic acid in pharmaceuticals has been reported by Chapman *et al.* (*38*). The method of Roe *et al.* (*164A*) involving reaction with dinitrophenylhydrazine followed by measurement of light absorption of the reaction product in sulfuric acid solution was found to be the most reliable under all conditions. The use of *peri*-naphthindanetrione hydrate in a spectrophotometric assay for ascorbic acid has been described (*57, 58*). The trione is reduced to a red compound by the vitamin.

Interferences by various members of the vitamin B complex in the reineckate method for the determination of choline may be overcome by precipitation of choline reineckate at controlled pH levels (*9*). Data are given showing the effect of increasing pH on the precipitation of the interfering vitamins and on recovery of choline from mixtures of the various B vitamins. A procedure for increasing the sensitivity of the colorimetric reineckate method for choline is described by Lovern (*124*). The chromium of the reineckate salt is oxidized to chromate, which is then estimated colorimetrically as the diphenylcarbazide complex.

A modification of the colorimetric assay of folic acid substitutes zinc amalgam as a reducing agent. Para-aminobenzoylglutamic acid is recommended as a standard in place of *p*-aminobenzoic acid (*106*). The effect of variables is discussed in detail.

A preliminary discussion of a new method for the colorimetric estimation of menadione concerns the treatment of an alcoholic solution of menadione with concentrated hydrochloric acid, cooling, diluting with ethyl alcohol, and measuring photometrically the stable red color which develops (*3*).

The Koenig reaction in which the coupling amine is sulfanilic acid represents still another modification of the colorimetric method for the determination of nicotinic acid (*180*). The fact that the reaction product with nicotinic acid gives approximately twice the color as it does with an equivalent amount of nicotinamide is the basis for a quantitative method for evaluating mixtures of nicotinamide and nicotinic acid (*181*). Mueller and Fox (*146*) have described in detail their ammonia method for the determination of nicotinic acid, a preliminary report of which has appeared earlier. This procedure exhibits high sensitivity and reasonably good precision. Reactions involved are the conventional Koenig ones and the steps of the procedure require a time control.

The aluminum chloride reaction with rutin to form a yellow color has been applied to the determination of this substance in tablets (*47*). The method is applicable in the presence of aminophylline, ascorbic acid, barbiturates, and mannitol hexanitrate. A check on the absence of quercetin is accomplished by paper chromatographic separation.

A report on some studies of acid activation of glycerol dichlorohydrin, nature of products of reaction of this compound with vitamin A acetate, and inhibitors of the reaction has been made by Allen and Fox (*2*). It is concluded that the reagent prepared by codistillation of antimony trichloride with glycerol dichlorohydrin is still the most satisfactory for vitamin A determination. The antimony trichloride reagent for the determination of vitamin A has been improved by distillation of discolored solid samples of the reagent under moderate vacuum—boiling point 140° to 150° C. at 10 to 15 mm. pressure (*147*). A 6% solution of antimony trichloride in chloroform provides a slower reaction rate with vitamin A and its esters, thus permitting a more accurate determination of the absorption of the reaction product (*31*). The extinctions thus obtained are lower per unit of vitamin A concentration than those obtained according to the U.S.P. XIV monograph (*189*).

However, the increased precision of absorption measurement made possible by the slower reaction rate appears to be an adequate compensation.

The ultraviolet absorption methods for vitamin A determination have received considerable attention since this type of spectrophotometric technique has become official in the U.S.P. XIV. It has been shown that solutions containing both vitamin A and tocopherols give abnormally low vitamin A values (*68*). The nonlinear absorption of tocopherols in the range of 310 to 334 mμ has been found to be responsible for the over-correction of the absorption as outlined in the U.S.P. monograph (*188*). The authors have established a technique for eliminating this difficulty by destroying the vitamin A present in the sample with 60% sulfuric acid. This concentration of acid does not apparently affect the tocopherol present so that a "blank" may be estimated after treating the sample with acid. The stability of tocopherols with respect to 60% sulfuric acid has been confirmed by Chapman and Campbell (*36*). Brown (*32*) has discussed the effect of small errors in the measurement of absorbancies of vitamin A on the results as obtained by spectrophotometric assay; this author also describes some specially constructed refluxing and extraction apparatus for use in the U.S.P. XIV method. A considerable increase in the precision of the method is shown to be possible with careful attention to the details of handling and measurement. A detailed report of studies of vitamin A measurement made by seven cooperating laboratories utilizing the geometric correction method has been made (*1*, *84*). These results, which were analyzed statistically, were for direct dilution of the whole oils tested in cyclohexane. It is pointed out in the latter paper that the correction assumes two facts: The vitamin A curve does not differ from that of all-*trans* vitamin A; and, the interference is linear at the three points used in the correction. Effort has been made to "quantify" the degrees of departure from linearity in terms of the accuracy of the results.

Ridyard (*164*) has made an analysis of the factors affecting the recovery of thiamine hydrochloride added to extracts in the determination of this substance. The effects of variation of sample and errors in volumetric measurements are shown to be considerable. The possibility of effects at the oxidation stage and interference with the emission of fluorescent light in the fluorimeter are considered.

In a series of four papers (*24-27*) Boxer and Rickards have described three methods for the chemical determination of vitamin B_{12}. Two of the methods are concerned with reactions of the 5,6-dimethylbenzimidazole nucleus to form a colored product, the absorption of which can be measured, or a fluorescent product which can also be used for the quantitative evaluation of vitamin B_{12}-containing samples. The latter method is considerably more sensitive than the former; however, both methods suffer from interferences, particularly in natural materials. The third method described by these authors is a very elegant procedure utilizing the fact that vitamin B_{12} reacts to liberate a mole of cyanide ion per mole of vitamin when exposed to intense visible light. These workers have developed a very sensitive modification of the colorimetric test for cyanide ion which permits estimation of millimicrogram quantities of this substance in solution. Thus, illumination of vitamin B_{12}-containing substances, aeration of the solution with nitrogen, collection of the cyanide ion in alkali, and colorimetric measurement of the entrapped cyanide permits a relatively accurate and precise method for estimating vitamin B_{12}. A procedure for the removal of volatile interferences is discussed in detail. Analogs of vitamin B_{12} which exhibit biological activity may be converted to cyanocobalamin by treating the samples with excess potassium cyanide; excess cyanide ion may be removed from the solution by aeration with nitrogen prior to illumination. This technique permits estimation of the analogs of vitamin B_{12} (cyanocobalamin) as well as the cyano form of the vitamin itself.

A similar method for the determination of vitamin B_{12} has been developed independently by Wijmenga and Hurenkamp (*196*). These workers utilized considerably larger quantities of the vitamin (100 to 200 micrograms) for a single determination; the reagent for detection and estimation of cyanide is less sensitive than that described by Boxer and Rickards.

Another method for the determination of vitamin B_{12} in biological material involves the polarographic determination of cobalt (*59*). In order to separate the cobalt which is present in the vitamin B_{12} complex from inorganic cobalt, the hydrolysis and extraction method of Fantes, Ireland, and Green (*61*) is used. The residue from the octyl alcohol extract is ashed, extracted with dithizone, again ashed and the cobalt determined polarographically. Under certain conditions the analysis can be made sensitive to 1×10^{-9} equivalents per ml.

The estimation of vitamin D in various mixtures has been the subject of an intensive investigation by Green (*78-83*). This worker has described a reaction of vitamin D with iodine trichloride. Halogenation of vitamin D (and some other compounds) by this substance in carbon tetrachloride solution liberates iodine. A titration procedure which involves addition of the reagent to the vitamin D solution until a peak iodine intensity is reached (as estimated photometrically) has been developed. Conditions for the quantitative separation of vitamin D from interfering sterols and vitamin A have been established; these involve removal of pro-vitamins and precipitable sterols by differential solubility, precipitation with digitonin under controlled conditions, and a chromatographic separation on floridin earth. The method has been applied to analysis of the irradiation products of ergosterol and to certain fish liver oils of a wide range of potency. These studies also concern comparative results as obtained with the antimony trichloride-acetyl chloride color reaction. Cox (*43*) also reports some observations on the spectrophotometric estimation of vitamin D.

A direct method for the α-tocopherol content of natural tocopherol concentrates makes use of the fact that a solution of sulfuric acid of specific gravity 1.767 extracts non-α-tocopherol from a 2% petroleum ether solution in the presence of sesame oil (*37*). The α-tocopherol remaining in the organic solvent phase may be measured by titration with standard ceric sulfate solution.

GENERAL

A simple apparatus for the amperometric titration of halides in certain pharmaceutical preparations is described by Mader and Frediani (*131*). This technique permits the individual determination of chloride, bromide, and iodide, and of mixtures thereof by direct titration with silver nitrate solution. The precision of the method varies from 0.1 to 3.0% depending on the halide concentration.

A colorimetric method for the microestimation for free formaldehyde is based on the reaction of this substance with phenylhydrazine hydrochloride, subsequent oxidation with potassium ferricyanide, and measurement of the absorption of the product at 520 mμ (*183*). Accuracy of the method is reported to be better than 2%; relatively large amounts of acetaldehyde, isobutyraldehyde, and benzaldehyde do not interfere. Oxidation of a reaction product of formaldehyde and *m*-phenylenediamine with potassium ferricyanide produces a stable yellow-orange color (*52*). Formic acid is reported not to interfere in this procedure.

In a microcolorimetric method for the determination of glycerol, Harvey and Higby (*91*) described procedures for the removal of proteins, sugars, lipides, and organic acids from biological filtrates. The resultant solutions are heated to 140° C. with 10% catechol and sulfuric acid, cooled, and the absorption of the solution measured at 510 mμ. It has also been noted by Radley (*163*) that anthrone dissolved in concentrated sulfuric acid develops a characteristic fluorescence when heated with low concentrations of glycerol, glycol derivatives, and tartaric acid.

A survey of possible interferences in the Karl Fischer method for the determination of moisture and the methods for their elimination has been presented by Mitchell (*142*). A very satisfactory primary water standard for use with the Karl Fischer method is sodium tartrate dihydrate (*150*).

Measurement of the concentration of polyoxyethylene stearate has been found to be possible through the formation of a complex with this substance and the amylose fraction of potato starch; the noncomplexed amylose present is free to form the characteristic starch-iodide complex which can be measured photometrically (*127*).

PHYSICAL METHODS

ALKALOIDS AND RELATED SUBSTANCES

It has been demonstrated that aspirin, phenacetin, and caffeine may be determined simultaneously by means of infrared absorption measurement (*155*). Codeine may also be estimated in combination with these substances by infrared absorption. Phenylpyramine is assayed in similar combinations by an ultraviolet absorption procedure. Jones and Thatcher (*104*) have utilized a preliminary separation of aspirin from phenacetin and caffeine followed by ultraviolet absorption measurements of the constituents in chloroform solution. Concentrations in the 2-component solution are calculated by simultaneous equations. A rapid and convenient procedure for the direct spectrophotometric determination of mixtures of these compounds has also been described by Mattocks and Hernandez (*137*).

Infrared absorption techniques permit the simultaneous determination of quinine and strychnine in elixir of iron, quinine, and strychnine phosphates (*191*). The authors also report a procedure in which the quinine is determined fluorometrically. The use of infrared spectra in the quantitative and qualitative determination of alkaloids is proposed by Pleat *et al.* (*162*), who have reported the spectra of 22 alkaloids in the range 3 to 14μ. Error in the quantitative measurement of alkaloids varies from 1 to 20% depending on the alkaloid concentration. Spectra were obtained from the solid alkaloids or their salts in a Nujol mull as well as from solutions in such solvents as chloroform, carbon tetrachloride, carbon disulfide, and mixtures of these. Similar quantitative infrared measurements are reported for the analysis of mixtures of cinchonidine-cinchonine, and quinindine-quinine (*160*).

Keenan (*107*, *108*) continues to report the crystal characteristics and confirmatory chemical tests of the important alkaloids; among those recently published are the hydrochloride, phosphate, salicylate, and sulfate of quinine, apomorphine hydrochloride, atropine, berberine, brucine, and strychnine. A direct ultraviolet absorption spectrophotometric procedure for the determination of caffeine and sodium benzoate involves dilution with ethanol (*93*). The usual 2-component system measurements are made at 228 and 272 mμ.

Several antihistaminic compounds have been examined polarographically and found to be reducible; however, the diffusion current waves were not found to be reproducible (*21*). The identification of derivatives of barbituric acid is aided by a table (*28*) giving the micro melting point and the refraction values of the melt for 22 barbiturates.

A polarographic method for the determination of digitoxin and gitoxin has been reported by Hilton (*96*). The average half-wave potential for digitoxin is −1.965 volts and for gitoxin −1.960 volts. Both drugs give diffusion current curves of such a type that low concentrations of the order of 2 to 20 micrograms % may be determined. Polarographic studies of strophanthidin, cymarin, *g*-strophanthin, and periplocin indicate that reduction of all these substances occurs at the same potential, apparently at the unsaturated lactone site (*174*). The ultraviolet and infrared absorption curves as well as the polarographic half-wave potentials for khellin, visnagin, and khelloglucoside have been described (*6*, *56*). Identification and assay methods based on these various physical properties have been established. The half-wave potential for *k*-strophanthin in alcoholic quaternary ammonium salt solution has been determined to be −2.3 volts. The detection limit is 0.4 mg. per ml. (*138*).

Stoll (*178*) has reviewed work relating to the structure, synthesis, isolation, and identification of the Ergot alkaloids. The partition of several of the Ergot alkaloids between ether or benzene and water at various pH values has been determined and separation procedures involving systematic extraction and counter current distribution have been devised (*92*).

ANTIBIOTICS

The crystal morphology, x-ray diffraction data, optical properties, pleochroism, and fusion data for aureomycin hydrochloride have been reported (*116*). The ultraviolet absorption curves of aureomycin hydrochloride and terramycin hydrochloride in different solvents have been described (*98*). Methods utilizing the ultraviolet characteristics and based upon the hydrolysis products of these antibiotics are utilized. Results compare favorably with the biological assay. Goldstein *et al.* (*77*) report a comparative study of the biological and chemical assay of aureomycin. The degradation of aureomycin hydrochloride in the presence of water is not reflected by chemical assays based on the yellow color developed with acid or by ultraviolet absorption measurements at 369 mμ. Dry degradation (heating at 200° C.) is reflected in decrease in potency as determined by the chemical assay.

A simplified direct spectrophotometric assay for benzylpenicillin makes use of the differences in extinctions at 263 and 280 mμ of the sample dissolved in 95% ethanol. Measurement of the absorption of the solution at 322 mμ detects decomposition or impurities. The precision is claimed to be ±2% (*158*).

Polarographic studies on streptomycin and mannosidostreptomycin indicate that their similarity of behavior probably precludes a simple polarographic technique for determining these compounds in the presence of each other (*29*).

CHEMOTHERAPEUTIC AGENTS

A polarographic method for the estimation of γ-1,2,3,4,5,6-hexachlorocyclohexane in lotions and ointments is reported to be quite rapid and to have an accuracy of ±2% or better (*67*). Kofler (*113*) has described a technique for the detection of traces of *m*-aminophenol in *p*-aminosalicylic acid. In this procedure antipyrine is added to *p*-aminosalicylic acid, with which it forms a eutectic at 55° C., and with *m*-aminophenol, below room temperature. The difference in eutectic temperatures may be used for the detection of this impurity.

Direct ultraviolet absorption measurements of the substances in methanol at 328 mμ may be used to determine the amount of Amithizone (*p*-acetamidobenzaldehyde thiosemicarbazone) in commercial preparations (*123*). The selective absorption of the —C—ONO$_2$ band is the basis for a method of determination of nitroglycerin by infrared spectroscopy (*159*).

HORMONES AND RELATED SUBSTANCES

The determination of pregnenolone and pregnenolone acetate by an infrared spectrophotometric technique is described by Papineau-Couture and Burley (*154*). Since these materials show no specific absorption bands peculiar to the entire molecule, measurements are taken at several intense peaks. Agreement between the peak values in terms of concentration is an indication of the presence or absence of impurities.

METALLIC IONS AND RELATED SUBSTANCES

A flame photometric technique for the estimation of calcium in certain biological fluids is claimed to possess an accuracy equal to that of the gasometric determination of calcium oxalate (*171*). Cobalt(III) is determined as trioxalatocobaltate in the presence of a large excess of nickel, copper, and iron as well as most other elements (*115*). Reduction to Co(II) occurs before the waves due to oxalate complexes of most other metals. Several official iron preparations have been examined polarographically and found to be assayable by this technique (*21*).

PROTEINS AND AMINO ACIDS

Efferse (*55*) gives an account of a method in which serum proteins are separated into 25 fractions by means of salting out with ammonium sulfate at a constant pH and temperature. The quantitative determination of the fractions is accomplished spectrophotometrically at 277.5 mμ; the procedure is far more rapid and requires less experienced assistance than nitrogen determination by the Kjeldahl method.

VITAMINS

Deuteronicotinic acid is prepared by direct exchange of nicotinic acid with deuterosulfuric acid. The compound is subsequently utilized in an isotope dilution procedure for the estimation of nicotinic acid. Infrared measurements serve to estimate the amount of tracer in the sample isolated (*186*). The extinction values of a highly purified vitamin A acetate (three times recrystallized from methanol) are given for ethanol, isopropyl alcohol, and cyclohexane solutions (*40*). These workers report that the absorption band is narrower than that reported by Morton-Stubbs and used in their geometric correction procedure.

Polarographic studies of vitamin B_{12} indicate the presence of one well-defined reduction wave at −1.12 volts versus standard calomel electrode. The potential is independent of the pH in the range 5.2 to 11.7 and has the same value in several electrolytes (*49*).

The infrared absorption spectra from 2 to 16 microns of the known tocopherols and of some of their chemical products have been presented (*165*). Absorption bands for differentiating the tocopherols from their chemical products are described. A polarographic procedure for the determination of 2-methyl-1,4-naphthoquinone (vitamin K_3) has been described (*203*).

GENERAL

The volume expansion of solutions containing 20 to 78% alcohol may be utilized in measuring the ethanol concentration. The sample is heated and the volume measured at two temperatures. The degree of expansion may then be related to the alcohol content (*119*). The temperatures at which 50:50 volume % mixtures of Chlorex (dichlorodiethyl ether) and various alcohols become completely miscible are termed Chlorex points, and are used for the identification and purity testing of alcohols (*187*). An infrared determination for the estimation of the ortho and meta isomers in *p*-cresol and the freezing points of the pure cresols are described by Knapp *et al.* (*110*). The infrared absorption spectra from 2 to 15 microns for several saturated and unsaturated fatty acids have also been reported (*175*). Organic acids may be solubilized in carbon disulfide and carbon tetrachloride for the purpose of measurement of infrared absorption by the addition of 0.5 to 2.5% triethylamine (*5*).

Extensive discussions of the various methods for the determination of moisture have recently appeared. These concern oven drying and chemical desiccation techniques (*200*), electrical measurement of water vapor using a hygroscopic film (*192*), and various distillation procedures (*64*). These surveys contain much useful critical comment concerning the application of known methods.

Among the outstanding new applications of analytical methods to the assay of pharmaceuticals and natural drugs have been those involving tracer methods. Isotope dilution procedures utilizing compounds labeled with radioactive or stable isotopes are proving to be particularly useful. Certain deuterated materials show distinct differences in infrared absorption from their normal counterparts. This fact permits the adaptation of isotope dilution techniques to equipment which is presently available in many laboratories. Radioactivity detectors or mass spectrometers are not then required in order to pursue studies involving tracer techniques.

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Natural and Synthetic Rubbers

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THIS is the fourth of a series of annual review articles to appear in this journal on analytical methods pertaining to natural and synthetic rubbers. The first review (*27*) covered only chemical methods, but the second (*25*) and third (*26*) were broadened to include physical testing.

The present review also covers both chemical and physical testing, and refers to articles appearing in the journals for the year ending about November 1951. Like the previous reviews, it omits test methods applied to compounding ingredients, except for their identification or quantitative determination when mixed with rubber. It also omits tests on materials used in the manufacture of synthetic rubbers. It does not in general refer to procedures that are more concerned with problems of fundamental research than with testing methods unless they employ unique apparatus or techniques which seem likely to prove to be of value in testing. Old procedures employed in recent publications for testing or research are not referred to unless they have been modified or improved. No references are made to the patent literature. This review is restricted to procedures that have already been applied to rubber, rather than to general procedures which may find future application in this field. Testing procedures which have in previous reviews been referred to from only their published abstracts, such as those presented at scientific meetings, are referred to again when the complete papers have appeared in the literature.

GENERAL INFORMATION

SURVEYS

Besides the review papers already mentioned (*25–27*) several other surveys have appeared within the past year. The Institution of Rubber Industry (*77*) has issued its "Annual Report of the Progress of Rubber Technology" for the year 1950, which is made up of selected reviews written by experts in the various fields of rubber technology, including physical and chemical testing of rubber and latex. In the past this annual publication has been months behind, but it now has been brought up to date. Rossler (*237*) issued her third annual rubber formulary, which comprises a system of recording data on rubber compounds in an easily accessible form. The information is arranged on 5 × 8 inch cards, which are coded according to the punched-card system. Current information is issued monthly to subscribers. The London Advisory Committee for Rubber Research (*164*) in its latest annual report describes work done on standardization of procedures.

In a series of review articles on chemical engineering materials for construction purposes Fisher (*94*) covered the general field of elastomers and Peters (*227*) surveyed that of hard rubber. Both authors referred chiefly to those properties of the materials which are important for purposes of construction, but they also made references to methods of physical testing. Straka (*278*) also refers to testing procedures and methods of low-temperature evaluation in an article enumerating the recent advances in the use of rubber in engineering.

Kreuter (*151*) continues a series of review articles on testing methods used in the rubber industry. In it he gives directions for the construction and choice of equipment for a rubber testing laboratory. Brown (*54*), in an article on instrumentation in rubber processing, describes weighing equipment, thickness gages, temperature control equipment, flexometers, penetrometers, and other items. Hader and le Beau (*111*) wrote a general article on reclaiming processes, in which they enumerated chemical and physical tests that are important in the reclaiming industry. The B. F. Goodrich Chemical Co. (*105*) issued a technical manual covering information on Hycar synthetic rubber, which includes a chapter describing compounding and test procedures recommended in the laboratory evaluation of Hycar compounds.

Three books (*23, 157, 182*), two of them in French and one in German, have been written on rubber manufacturing and technology. All were written especially for instruction of young rubber technologists, and include chapters on the physical and chemical testing of rubber.

For the past 10 to 15 years the Research Association of British Rubber Manufacturers has been issuing bulletins on certain research work to members only. The association no longer considers the information in these bulletins as confidential. It does not, however, expect to publish all these bulletins in full but has decided to release the information, and the existence of these papers has now been made known by abstracts in the May 1951 issue of *Summary of Current Literature* (*279*). Those reports which are concerned with rubber testing are referred to in the appropriate sections of this review article.

STANDARDIZATION

Committee D-11 (Rubber and Rubberlike Materials) of the American Society for Testing Materials issued another book on standards for rubber products (*4*), which contains nine revised procedures and three new ones. The latter are D 1147-51T on a method of test for compressibility and recovery of gasket materials, D 1148-51T on a method of test for discoloration of vulcanized rubber, and D 1149-51T on a method of test for accelerated ozone cracking of vulcanized rubber. The Research Association of British Rubber Manufacturers (*185*) issued a circular giving details of 160 British specifications for rubber goods.

The results of three meetings of the International Organization for Standardization, Technical Committee 45 on Rubber (I.O.S./TC/45), in London (1948), in The Hague (1949), and in Akron (1950), have been described, along with the work outlined for the 1951 meeting in Oxford (*131*). Various accounts (*38, 56, 132, 235, 239*) have been presented of the successful Akron meeting, at which a number of test procedures were discussed and adopted.

The Bureau of Ships of the United States Navy (*291*) has issued a rubber formulary which includes 71 recipes covering 26 specifications relating to products purchased by the Bureau of Ships.

CHEMICAL ANALYSIS

X-ray diffraction methods have been applied by Goldspiel and Bernstein (*104*) to the identification of natural and synthetic rubbers. They studied elastomer stocks at room temperature, at lower temperatures, in the stretched, unstretched, aged, and unaged states, and with combinations of these conditions. They were able from analysis of the results not only to identify natural and various synthetic rubbers but also to estimate quantitatively the crude rubber content of mixtures. A review article (*140*) in German refers to several methods used in the identification of natural and synthetic elastomers, and then discusses in more detail the well-known methods of Burchfield. Parker (*220*) examined some of the methods for identifying synthetic rubbers, and elaborates on the chemical analysis for nitrogen, chlorine, sulfur, the swelling ratios, the rate of breakdown in acids, and on other methods now in use.

Sands and Turner (*247*) developed some rapid methods for preparing samples of rubber for spectroscopic study in the solid state. The technique consists of laminating the sample between two sheets of other materials which have a transparent region in the infrared. As an example of rapidity and precision of the method the authors were able to determine the acrylonitrile content of a nitrile rubber in 15 minutes with a probable error of 1%. Mann (*177*) also discussed practical methods of quantitative analysis of elastomers using the method of infrared spectroscopy.

Mann (*178*) also applied his infrared spectroscopy to the identification of accelerators and antioxidants in vulcanizates. He presented a scheme for such analysis which involves their extraction from the rubber, their separation by means of chromatography, and then their identification spectroscopically. Another spectrometric method was developed for accelerators by Kress (*150*), in which a chloroform solution is measured for optical density at several selected wave lenths in the ultraviolet depending on the type of accelerator. The method is fairly rapid and the precision is said to be good. Budig (*55*) identifies accelerators in rubber by visual observations of their chemical reactions. Several Russian investigators (*64, 153*) continued earlier work on methods of identification of these same materials.

The quantitative method for the determination of the rubber hydrocarbon content of natural rubber by the bromide method has been improved by Gowans and Clark (*107*). They found that the addition of chloroform to the bromination mixture prevents the undesired bromine substitution reaction and has no apparent bad effect on the desired addition reaction. The empirical conversion factor from the rubber bromide to natural rubber has now been brought very close to the theoretical value. Another method for the determination of hydrocarbon content was developed by Fanning and Bekkedahl (*90*), which makes use of refractive index measurements of a known weight of acetone-extracted rubber in a known weight of 1-bromonaphthalene. Both this method and the bromide method have the disadvantage that they are not applicable to rubbers that have been vulcanized, nor can they be used where there are mixtures of natural and synthetic rubbers.

A modification in design of the ASTM rubber extraction apparatus has been made by Dyer (*80*). The precision of the determination of acetone extract by the method of the British Standards Institution has been the object of a study by Foxton and Wake (*98*).

Linnig, Milliken, and Cohen (*162*) describe a rapid method for the determination of ash in GR-S synthetic rubbers and latices. They found no loss of ash on introducing the sample directly into the furnace at 550° C., provided that filter paper is wrapped around the rubber sample or filter pulp is used to absorb the latex in a cone of filter paper inside the crucible.

Kirstev (*145*) describes a new method for the determination of sulfur in rubber. The sample is oxidized by a stream of oxygen at 1100° C. The resulting gases are reduced by hydrogen, and the sulfides and polysulfides which are formed are determined by oxidimetry. The results obtained by this method are low and must be corrected. Poulton and Tarrant (*231*) determine the quantity of free sulfur in vulcanizates by a polarographic method. Siegfriedt, Wiberley, and Moore (*262*) determine sulfur by a micromethod after a 2- to 200-mg. sample of rubber has undergone combustion in a 40-ml. oxygen bomb. The bomb washings are titrated with barium chloride solution using tetrahydroxyquinone as indicator. A single determination does not require more than 1 hour total elapsed time. Agazzi, Parks, and Brooks (*2*) independently developed a similar bomb and used it successfully for determining both sulfur and chlorine. They also report a significant saving in time.

An extensive review of the literature on the determination of minute quantities of copper in rubber has been made by van der Bie (*34*). He recommends a procedure which involves ashing the rubber sample, and describes some modifications of the usual diethyldithiocarbamate method. Ebe (*82*) improved the accuracy of an older colorimetric method of Shimada for copper determination in vulcanized rubber, which makes use of thiocarbanilide in a chloroform solution. Lee, Weiss, and Hoffmann

(*158*) object to the present methods of analysis for copper, in that they report the total quantity of copper, and recommend that the methods be changed to determine only the ionic or injurious copper. They therefore present a method which reports only that copper which is deleterious to the aging of rubber.

The direct determination of oxygen in organic compounds by the thermal decomposition method of Unterzaucher and Schulze has received considerable attention during the past year. A round-table discussion (*3*) was held by the Division of Analytical Chemistry, AMERICAN CHEMICAL SOCIETY, at which time most of the investigators reported satisfactory results from the procedure. The method was reported to be basically sound, but the conditions of experiment must be observed carefully. Several investigators (*66, 78, 123*) made modifications in the procedure so as to correct for small errors.

Heinisch and van der Bie (*119*) studied the foreign material or dirt in rubber, and suggest drawing a distinction between the total or absolute dirt content and the "harmful" dirt. They propose as a definition for the harmful dirt that portion of the total dirt which is retained on a 325-mesh screen. The authors give a short general survey of the present methods used in their laboratory for the determination of dirt, and describe an improved gravimetric procedure which is suitable for routine work. Van Essen (*87*) also outlines a rapid method for the determination of the dirt content in rubber. The Crude Rubber Committee of the American Society for Testing Materials (*5*) has been attempting to evaluate three different methods for dirt determination.

Kolthoff and Medalia (*147*) review the various methods used by other investigators to determine organic peroxides in organic materials including rubber. They report that the methods involving reaction with ferrous iron are inherently less accurate than the iodometric methods, but that for purposes of control work, where only relative values of peroxide are required, the ferrous methods may be of particular value.

Medalia and Kolthoff (*183*) show that the conventional solubility determinations give no information regarding the microgel content of a polymer unless the polymer has been subjected to the appropriate preliminary treatment. They recommend a standardized procedure of milling and heating the polymer prior to the solubility determination in benzene by some static methods.

Ebe (*81*) developed a method for the quantitative determination of carbon black in vulcanized rubber which utilizes the oxidizing power of chromic acid. He successfully applied it to insulated wire, tire treads, reclaimed rubber, and other compounds. Hammond (*112*) describes a method in which the acetone- and, chloroform-extracted rubber is treated with nitric acid, kieselguhr and carbon tetrachloride are added, and the solid material is filtered on to a Gooch crucible, which is dried to constant weight, and then heated in a furnace to burn off the carbon. Boettcher (*41*) used the electron microscope technique to study the dispersion of carbon black and other fillers in a compounded rubber batch or in a vulcanizate. The examination may be performed directly on microtome sections or on extremely thin vulcanizates.

Arnold, Madorsky, and Wood (*10*) developed a simple method for the measurement of refractive index of elastomers by means of the Abbe-type refractometer. The rubber is purified by extraction, dried in a vacuum oven, and pressed between aluminum foil at 100° C. before it is placed on the prism of the refractometer. The standard deviation of measurements corresponding to intrinsic variability of the method was 0.00007. Other investigators (*14*) also report a new and simple method for the determination of refractive index of transparent solids. The method involves the use of inexpensive materials, but gives results only to the second decimal place.

Been, Grover, and Ewing (*22*), in evaporating off the solvent from rubber cement as described by ASTM method D 553-42 (*4*), found that the addition of 0.5 gram of a silicone oil to the cement keeps it from foaming and forming a rubber film during distillation.

Best and Moakes (*30*) describe methods of detecting and estimating wax bloom on the surface of a rubber vulcanizate. A "wax detector" is illustrated which heats the surface while a visual examination is being made by means of a reading lens.

DeNeef (*204*) was able to identify natural rubber which had been coagulated with too great a concentration of sulfuric acid. Aging properties, determined both visually and by tests on plasticity, were evaluated after heating smoked sheets for 3 hours at 140° C. or crepes for 7 hours at 110° C. Considerable softening of the rubbers takes place from the above heat treatments if too much sulfuric acid has been used in the coagulations.

AGING AND DETERIORATION

Two short review articles (*30, 130*) were prepared on the published literature on atmospheric and ozone attack on rubberlike substances. Another paper by Ford and Cooper (*96*), in addition to giving a review of previous work on aging, describes a thorough study of the factors affecting the weathering of rubberlike materials. They consider ozone to be the prime cause of weather checking of rubber, and believe that light, heat, and moisture are contributing factors of secondary importance. They describe a weathering apparatus which has considerable flexibility. It can expose rubber strips to controlled test conditions under both static and dynamic elongations. The ozone concentration, the temperature, and the relative humidity can be controlled to within narrow limits over a wide range of conditions. A system of lights and filters makes possible a wide coverage of the light spectrum.

Shaw and Adams (*260*) made rubber aging tests in which physical properties of test specimens were measured at intervals while undergoing aging. They were able to evaluate the extent of ozone cracking by making electrical conductivity measurements on T-50 type specimens while they are stretched in a fixture and exposed to ozone. They also correlated ozone aging with strain data obtained at a given stress at varying intervals of time on the same specimen while undergoing ozone treatment.

A Symposium on Ozone Cracking was held at a meeting of the Division of Rubber Chemistry of the AMERICAN CHEMICAL SOCIETY, at which time six papers (*19, 71, 230, 244, 290, 304*) were presented. Winkelmann (*304*) stated that ozone cracking on outdoor aged samples can be duplicated in an ozone chamber, but as outdoor exposure is also affected by sunlight, heat and humidity, many tests and much good judgment must be exercised in correlating accelerated and outdoor exposure tests. Bartel and Temple (*19*) studied the ozone concentration in Los Angeles and the surrounding area, and decided that the rubber checking in this area is caused by the ozone concentration of the air rather than by the smog.

Rugg (*244*) analyzed the depth, width, length, and number of the cracks caused by ozone deterioration, and proposed as the most reliable method a procedure which measures the depth of the cracks by means of a low-power microscope having a graded scale included in the field. Cuthbertson and Dunnom (*71*) studied the effects of temperature and elongation on the cracking of natural rubber and GR-S in ozone, and found that the cracking threshold, which they define as the elongation below which no cracking occurs, decreases with increasing temperature.

Thompson, Baker, and Brownlow (*290*) studied the factors affecting the results of ozone exposure tests and the effect of compounding ingredients on the ozone resistance of neoprene vulcanizates. They concluded that accelerated ozone testing should be considered as indicative rather than an absolute measurement of actual resistance to attack. The Research Association of British Rubber Manufacturers (*233*) states that in designing an apparatus for evaluating weather cracking two causes must be separated. For light-catalyzed oxidation a carbon arc is necessary to produce the effects of the sunlight, and either a high-voltage discharge generator or an ultraviolet light is required to produce ozone oxidation.

This past year the American Society for Testing Materials (*4*) adopted a tentative method of test (D 1149-51T) for accelerated ozone cracking of vulcanized rubber. Best and Moakes (*29, 30*) give a description of an apparatus designed for tests of exposure cracking at controlled temperatures and concentrations of ozone. Stanley and Allison (*273*) applied the infrared spectrographic technique to the study of ozone deterioration, and present spectrograms representing different degrees of ozonization for each type of polymer. Popp and Harbison (*230*) discovered that neither the type nor the particle size of carbon black has any effect on the rate or degree of cracking in polymers when exposed to sunlight or ozone under static stress.

Pedersen (*225*) modified the original oxygen absorption apparatus of Dufraisse, and states that the manometric method for evaluation of the oxidation of rubber is of great value with respect to reproducibility of results and for the purpose of studying the effects of antioxygenic agents and of rubber poisons such as copper and manganese. Shelton and Cox (*261*) compared the volumetric oxygen absorption test with air oven aging and the oxygen bomb tests, and came to the conclusion that the oxygen absorption test has a greater potential value than the other two methods. Blum, Shelton, and Winn (*39*) state that because of a finite rate of diffusion of oxygen in rubber, the conventional 0.075-inch thickness of rubber specimen is too great for studies of the effects of variables such as molecular structure, vulcanizing agents, antioxidants, etc., on the oxidizability. They present data to aid subsequent investigators in the selection of approximate safe limits of thickness in studying oxidation and aging at various temperatures for both the constant rate and the autocatalytic stages of oxidation. The oxygen absorption method was thought by Parks, Cole, and D'Ianni (*221*) to be successful in comparing the stabilities of GR-S polymers prepared by the mutual polymerization process. Baxter, Morgan, and Roebuck (*21*), on the other hand, believe that inaccurate conclusions may be obtained if aging is to be judged only by oxygen absorption. They describe and illustrate a new apparatus with which the oxidation of the rubber can be studied by simultaneous measurements of absorption of oxygen at constant pressure and of stress-strain properties at low elongations during aging of a single vulcanized rubber sample under closely controlled conditions.

McGavack and Bevilacqua (*170*) studied the absorption of oxygen by ammonia-preserved rubber latex and found that the rate of oxidation is dependent on the pH of the latex, bacterial activity, and temperature. The oxygen is absorbed not only by the rubber itself but also by the nonrubber constituents of the latex.

Eccher and Oberto (*84*) present details of two aging ovens which they claim are improvements over the conventional ones. Both are cylindrical in shape. One of them is heated and controlled electrically, while the other is surrounded by a jacket containing the vapors of a suitable liquid for temperature control, ethyl alcohol being very convenient for maintaining a constant temperature of 78° C. In the latter the air in the oven is circulated by convection, and in the former it is moved by a fan. The authors show that an antioxidant is more likely to be conveyed from one vulcanized sample to another in an aging oven when the air is circulated than when the air is at rest. Fackler and Rugg (*89*) studied the migration of materials during accelerated aging by the oxygen pressure method and show that the results of test may be grossly misleading. Apparent resistance to oxidation may either be increased or decreased, depending on the nature of the migrating material. Serious consideration should be given to the use of individual bombs for different materials as a means of obtaining more reliable results.

Soden and Wake (*267*) studied the deterioration of rubber under the influence of light as well as dry and moist heat. They compared results from aging in dry and in moist tropical locations with those obtained from oven aging under both dry and humid conditions. They were able from the results of their accelerated aging to assess the behavior of rubber in the tropics. Hofmeier (*122*) suggests that greater sensitivity is obtained for weathering tests if a high ratio of the area of a test specimen to its volume is used.

Vacca, Erickson, and Lundberg (*293*) found that accelerated aging of black neoprene jackets in air at temperatures up to 100°C. gives results more comparable with outdoor aging as regards decrease of elongation than do other tests. Okita, Sakita, and Mizoguchi (*217*) found that accelerated aging at 100° C. for 1 day corresponded to natural aging for 1 year for wire vulcanized with tetramethylthiuram disulfide alone and to 4 years for ordinary sulfur-cured rubber wires.

Pedersen and Nielsen (*226*) give details for the construction of a simple balance for the measurement of stress relaxation at constant elongation. Results from work using this balance show that stress-relaxations give approximately the same estimate of stability as does the normal Geer oven test.

Bateman and Gee (*20*) studied olefinic oxidations, including rubber, and derived expressions to evaluate separately the propagation and termination rate constants. D'Or and Kössler (*218*) used infrared spectroscopy to study the oxidation of natural rubber by following the variations in concentration during oxidation of the various groups or radicals as they combine with oxygen. O'Brien (*216*) found that a general relationship exists between the electrostatic contact potentials of rubbers and their susceptibility to oxidative reactors involving sunlight, flexing, and ozone.

Salomon (*246*) makes the statement that the service life of rubber articles should be determined from dynamic aging because static tests do not give sufficient indications.

Buist and Williams (*61, 62*) gave a general review of the mechanism of flex cracking and described the various tests employed to evaluate this property. They stressed the importance of distinguishing between the two processes, crack initiation and crack growth. Because of a great variability in the results of cut-growth testing with apparently identical samples of rubber, Buist and Powell (*60*) developed an improved needle which gives superior performance to the cut-growth test as regards reduction of variation between samples. Newton (*207*) made a study, using the DeMattia machine, of the time intervals at which the machine should be stopped for examination of the state of cracking of the samples, and found that less frequent observations may be made on them without sacrificing accuracy.

The British Rubber Producers' Research Association (*50*) states that a quantity can be derived expressing the tendency of a rubber to undergo cut growth. This quantity is characteristic of the rubber and is independent of the shape of the specimen or the type or position of the cut. It thus becomes possible to relate the results of different tear tests and also to assess their efficiency in determining tendency to undergo cut growth.

LATEX

At a recent meeting of the AMERICAN CHEMICAL SOCIETY, Murphy (*203*) outlined the established methods for evaluating the chemical and physical properties of latex, and also described newer methods of testing and their applications. The Rubber Stichting (*243*) in Holland issued a revised edition in German of its booklet on latex. The British Standards Institution (*52*) revised the part of its old testing manual on latex, BS 902, which deals with sampling and basic tests. The R. T. Vanderbilt Co. (*294*) describes the methods used in its laboratory for the testing of rubber latices, which are, in so far as possible, designed to follow standard ASTM procedures. The London Advisory Committee for Rubber Research (*164*) describes its work on the standardization of tests for latex. It particularly relates to mechanical stability tests, viscosity, and the quantitative determination of copper and manganese. A new book on the physical chemistry of latex by Kopaczewski (*148*) describes test methods and contains an extensive bibliography on latex. Martin (*179*) describes the results obtained from discussions on latex testing at the first three meetings of the International Organization for Standardization.

A detailed critical review is presented by Messenger, Parris, and Pinkney (*186*) on the methods of testing mechanical, chemical, and thermal stability of natural rubber latex. Kraay and van den Tempel (*149*) presented a paper summarizing the testing of the stability of latex to zinc oxide. Klaxon Ltd. (*146*), describes a high-speed machine which it developed, in conjunction with the London Advisory Committee for Rubber Research for the determination of mechanical stability of latex. Miserentino (*188*) developed a new method for measuring the mechanical and the chemical (zinc oxide) behavior or stability of latex. The test is based on the determination of volume-time froth curves produced by whipping a known amount of latex of normal operating concentration at a constant speed and controlled temperature.

The Brookfield viscometer now has an attachment, called the UL adapter (*53*), which makes possible more precise measurements in the ultralow viscosity ranges. Sutton (*281*) uses a torsion type of viscometer for measuring viscosities because it is inexpensive and still suitable for works control purposes.

Van den Tempel (*287*) states that the mean particle size distributions of rubber globules are of considerable technical importance, as they determine the behavior of latex during creaming or centrifuging and therefore have a bearing on stability and on viscosity. He also says that the use of visible light to determine the particle size or particle-size distribution in Hevea latex renders the results meaningless, as only about 40% of the particles have a diameter of more than 0.2 micron. Yudowitch (*309*) constructed a high resolution camera for small angle x-ray scattering which he found to be very useful for measuring particle sizes of latices from x-ray diffraction peaks.

Van Essen (*88*) devised a rapid method for the determination of the average molecular weight of the rubber in Hevea latex. A stabilizer is first added to the latex. A small portion of the diluted latex is shaken with a mixture of toluene and pyridine until the rubber is dissolved in the solvent. A viscometric method is used to obtain the average molecular weight. The procedure is useful at plantations to study the trees, methods of tapping, and other problems.

Khoroshaya and Avilov (*143*) developed a rapid colorimetric method for the determination of the pH of carbon black–latex mixtures. The procedure uses the pencil colorimeter, which the authors claim gives an agreement of 0.2 pH with the values obtained using a potentiometer and glass electrode.

Sutton (*281*) gives a technique for casting a film of rubber from latex for test purposes. He recommends pouring the latex on glass plates, drying the rubber at room temperature, and then storing it in a desiccator for 6 days or more until the weight is constant before the tests are made on it.

UNVULCANIZED RUBBER

Under this general heading are included not only tests applied to unvulcanized rubber but also tests to determine characteristics of the process of vulcanization.

MOLECULAR PROPERTIES

The literature is reviewed by Hine and John (*121*) on the use of the ordinary microscope, the ultramicroscope, the ultraviolet microscope, and the electron microscope in the rubber industry. The limits of resolution of these instruments are discussed and the techniques of their use are described. Their chief use is to study the nature of latex, the structures of unvulcanized and of vulcanized rubbers, and compounding ingredients and their dispersions in rubber. Oberto (*215*) examined rubber test specimens under polarized light to find optical evidence of the presence of anisotropy caused by movements of particles during calendering, extruding, or molding operations. He used a microscope at low magnifications to examine microtome sections of the rubber. Transparent vulcanizates can be used to study the particle orientation, but greater detail is visible if a small quantity (1%) of carbon black is present.

Burgova and Korotkov (*63*) describe their infrared spectroscopic technique to determine the relative number of bivinyl structures, $CH_2CH:CHCH_2$ and $CH_2CH(CH:CH_2)$, contained in a polymer molecule. The results of their analysis are in good agreement with those involving chemical analysis by oxidation methods. By means of x-ray diffraction patterns and infrared absorption spectra, Schlesinger and Leeper (*250*) were able to identify both cis and trans forms of polyisoprene in a sample of chicle obtained from tapping a single tree. Sutherland and Jones (*280*) applied polarized infrared radiation to problems of molecular structure of natural rubber and gutta-percha. The spectra of the two were similar, but not identical in the amorphous state, but markedly different in the crystalline state.

Hermans (*120*) compared the results of the determination of the crystalline portion in a macromolecular system by means of x-rays with those obtained from density and from heat-capacity measurements, and reported them to be in good agreement. Work (*308*) determined the degree of crystallinity in natural rubber by means of dilatometric measurements. The degree of crystallinity was calculated from the change in expansivity on crystallization above the second-order transition and the expansivity below the transition. For determining the expansivities the author designed an automatic photoelectric recording interferometer (*307*), which he has used successfully in the temperature range from −185° to +185° C. to a precision of ±5% and in locating second-order transition temperatures to a precision of ±0.5° C.

Boonstra (*43*) found that the degree of crystallization as calculated from the temperature coefficient of elastic tension agrees reasonably well with that obtained from direct x-ray measurements. Campbell and Allen (*67*) studied crystallinity of various types of rubber in the unstretched state by means of a polarizing microscope and found the results to agree well with those obtained from dilatometric measurements. Both methods are more sensitive than the method of x-ray diffraction for detecting small amounts of crystallinity in high polymers.

Boggs (*42*) shows that the methods of statistical mechanics which have been applied successfully to the study of liquids can be modified appropriately to describe the behavior of rubber. A detailed calculation of the modulus of rubber as a function of temperature shows that the theory predicts a sharp increase in the modulus at low temperatures.

Witte and Anthony (*305*) employed the stress-temperature method as a means of studying the apparent second-order transition of polymers. A pronounced stress relaxation was observed to take place in the temperature region of this transition, which agrees favorably with that obtained from volume dilatometric studies. Forster and Anthony (*97*) supplemented the stress-temperature and volume-temperature experiments with a study of the length-temperature behavior of rubbers. Their test specimens were stretched to various initial lengths under constant loads at 40° C., and permitted to creep until the rate of change of length became small. On lowering the temperature in steps through the transition they found that the initial extension had an effect on the second-order transition.

Holroyd, Codrington, Mrowca, and Guth (*124*, *125*, *194*) describe a method of studying the structure of high polymers by measuring the line widths in nuclear magnetic resonance experiments. These line widths change appreciably through a temperature range in which a transition takes place from the soft rubbery state to the hard glassy state.

Weir (*301*) made compressibility measurements on polymers up to 10,000 atmospheres' pressure. From volume-pressure curves he found it possible to observe second-order transitions by marked changes in the slopes of the curves.

Ladd and Ladd (*155*) obtained direct evidence of carbon gel complex in rubber by means of an electron microscope. They developed a new technique to photograph and distinguish among sol rubber, unpigmented gel rubber, and the carbon gel complex itself. Pechkovskaya, Pupko, and Dogadkin (*224*) also used the electron microscopic technique in studying the structures and properties of a butadiene rubber loaded with carbon blacks.

VISCOSITY AND PLASTICITY

Stenzel (*275*) describes and illustrates a laboratory rapid-action plastometer evolved by Behre, which is easy to operate. The rubber is warmed to 70° to 80° C. and extruded through a narrow nozzle. After a definite time of extrusion at constant pressure the extracted strip is cut off and weighed. The swelling of the strip can also be measured to give an indication of the nerve.

The original design of Hoekstra's plastometer was modified by Binney and Smith and Ashby, Ltd. (*35*), and adapted for factory use. It is an instrument of the parallel plate type which compresses the sample to a fixed thickness at 100° C.

Eccher (*83*) describes a cylindrical rheometer of the Couette type which he has adapted to the determination of the rheological properties of extruded rubber and rubber mixtures. It was designed to provide data that could not be obtained with existing plastometers.

Taylor and Ball (*286*) discuss briefly the reliability of the various methods for temperature measurement and control during the Mooney test. They show the relationship among temperatures indicated by the thermocouples conforming to the design specified by ASTM designation D 1077-49T (*4*), temperatures indicated by a thermocouple coiled in the test specimen, and temperatures in the platens and dies. Their work shows that the measurement of temperature at specified points in platens, dies, or die holders may be satisfactory for control testing but is not adequate for obtaining comparable temperatures from one machine to another. Accurate control of temperature is extremely important. Whorlow (*303*) measured the temperature rise while shearing unvulcanized rubber at high rates in the shearing cone viscometer and showed that it is about twice that which is to be expected from simple theoretical considerations. This may have no serious effect on control testing, but may influence the results, especially in scorch testing.

A series of articles was prepared by Baader (*13*) in which he presents a critical review with discussion of the Defo instrument for measuring the viscoelastic properties of unvulcanized rubber. From these measurements he claims to be able to estimate the processing characteristics of rubber.

Mullins and Whorlow (*201*) state that the measured value of plasticity of a compounded rubber stock is not a definite characteristic of the stock but depends upon the whole past history of the sample. Either the complete history of the test sample should be closely controlled or the sample should be conditioned so that the properties are substantially independent of differences in its history. Tests on a number of samples of natural rubber show (*302*) that the Mooney viscosity cannot be predicted from measurements made by means of the Williams instrument.

Heinisch (*118*) determined the natural fluctuations in the plasticity or viscosity of crude rubber and found that they may be caused by biological or physiological factors, processing, time of storage, and the presence of materials such as copper or manganese, mildew, or microorganisms.

Bestul, Decker, and White (*33*) made comparisons of the viscosities of rubbers obtained with the Mooney viscometer (a shearing disk type) and the McKee Worker-Consistometer (a piston-type capillary viscometer) at various rates of shear. The agreement between the two instruments in their common range varied within 2 to 20% for different rubbers. The disagreements were probably due to factors such as hydrostatic pressure, elasticity, and slippage at the instrument surfaces.

Bestul, Belcher, Quinn, and Bryant (*31, 32*) studied the flow behavior of polymeric solutions of various concentrations by means of the McKee Worker-Consistometer at various rates of shear. They noticed that as the polymerization temperature of GR-S is lowered the flow behavior of its dilute solutions becomes more Newtonian. Schremp, Ferry, and Evans (*251*) describe a coaxial cylinder apparatus which serves to measure the apparent viscosity of a concentrated polymer solution at various shearing stresses and to follow the relaxation of stress after sudden cessation of flow. Müller (*195*) describes an apparatus which he used for studying the changes in elastic modulus of high polymers, including rubber, on periodic deformation.

MISCELLANEOUS

Van Amerongen (*7*) revised his earlier methods for obtaining greater precision in the determination of permeability of polymers to gases. In his studies he measured not only the permeability but also the diffusibility and the solubility of the gases. Barrer (*18*) made an extensive review of diffusion in elastomers, in which he outlined membrane methods for determining diffusion and solubility coefficients. Bächle (*15*) continued his earlier work on the swelling capacity of latex films in water.

Kirstenbaum, Hoffman, and Grosse (*144*) demonstrated an autoradiographic technique which makes use of carbon 14 in studying the distribution of carbon black in rubbers. The method proved to be superior to the microphotographic technique.

It also has an advantage over the tensile method in that it involves no breakdown of the rubber, which causes a variation in the results in the tensile procedure.

Glazer (*103*) employed dilatometric measurements to study the rate of vulcanization of crepe rubber by means of sulfur monochloride. A decrease in volume of the mixture during vulcanization enabled the author to study the reaction quantitatively. Kainradl (*139*) made a study of the vulcanization reaction as it takes place in the factory, and developed a laboratory technique for estimating the time and temperature for an optimum factory vulcanization from curing data obtained in the laboratory. Ball and Randall (*17*) made a thorough study of the rate of cure of present-day whole-tire reclaimed rubber in which they used and compared five criteria in determining the rate: Mooney scorch, tensile properties, energy capacity from stress-strain curves, elongation at constant load, and compression set.

Morley and Scott (*190*) showed that when the vulcanizates are left in contact with the hot mold and cover plates at the end of the prescribed vulcanization period, the vulcanizing reaction may be materially prolonged, which will give erroneous results. Scott (*254*) concluded from experiments that except for mixes containing highly active accelerators, storage up to 3 days before vulcanization is unlikely to cause changes in properties greater than experimental errors. He (*253*) also found on employing various pressures from 100 to 445 pounds per square inch on the mold during vulcanization that the tensile strength appeared to decrease with decreasing mold pressure. Hardness and resilience did not seem to be affected by this variation in pressure on the mold.

Leeds & Northrup Co. (*159*) report a unit that measures roll-surface temperatures. The measuring head is situated near the roll surface, and air is sucked past the measuring element. The equipment does not touch the film on the roll and consequently cannot damage it. It operates independently of surface speed, emission characteristics, and finish of surface.

Lunn continued his earlier study on safe working conditions on horizontal two-roll mills. He first made a graphical examination of mill roll conditions (*165*) which is an elementary practical development of an earlier theoretical contribution. Details were later given (*166*) of the mechanics and design of a sensitive safety bar for the mills, which is supposed to operate on an emergency independent of any voluntary or controlled effort in the part of the operator. Practical problems and illustrations were also given (*167*) relating to various sizes of rolls, including the 6-inch laboratory size. The maximum reach for safe working on a given mill can be determined precisely. Both the machine and the men operating the machine were considered in the calculations.

Cuthbert (*70*) and Stopforth (*277*) also worked on the safe working conditions on mills of similar type. A knowledge of certain body measurements, such as the shoulder height, the reach of the operator, and other measurements on the arm are necessary (*277*). A simple mechanical device is described (*70*) which records the distance of travel of the roll surface between operation of the brake by the safety bar and stopping the roll. Poynton (*232*) describes a safety device for use with laboratory-size rubber mills which is intended to operate before an accident can occur. A swinging gate of transparent material is placed over the front roll with but 1-inch clearance, which allows the sheet but not the hand to pass through. Rotation of the gate operates a switch which stops the mill.

The Wabash Metal Products Co. (*298*) announced a new 30-ton laboratory press, known as Model 30-11, which has a 6-inch stroke and 20-inch daylight opening. The manufacturer claims it has especially good paralleling of platens.

Shaw and Co., Ltd. (*259*), manufactures a new laboratory calender which has individually driven variable-speed rolls. Any desired roll speeds are obtainable by means of push-button controls.

A thickness gage, known as the Elcometer, is being produced by the Henry A. Gardner Laboratory (*101*). It is a self-contained unit and does not require any outside source of power. Industrial Nucleonics Corp. (*133*) manufactures a thickness gage which makes use of the radioactive materials, and includes a beta-ray radiation source, a radiation detector, and a recording device. Other thickness gages, also described in the literature (*11, 142*), make use of radioactive materials.

Several papers on refractive index measurements on rubber (*10, 14*) and rubber solutions (*90*) are referred to in the earlier section on Chemical Analysis because of their importance in that field.

EVALUATION AND GRADING

Representatives of the rubber-producing industries of the Far East held a meeting under the auspices of the Rubber Research Institute of Malaya in Kuala Lumpur in September 1949 with C. E. T. Mann as chairman. The proceedings of this interesting meeting, which were published the following year (*242*), contained the discussions involving the quality and the grading of crude natural rubber. McColm (*169*) emphasized the necessity of improving the quality and uniformity of natural rubber in order to stand competition with the synthetic product. Mann (*175*) admitted the necessity of expanding technical testing facilities at the plantations and of introducing some type of technical system of grading the rubber. Besides the general discussions, the sessions included presentation of several technical papers (*37, 73, 87, 95, 204*), which are referred to in various sections of the present review article. The proceedings of the meeting also include an abridged translation of a French article (*134*), which was the first to recommend the classification of the rubber into nine grades based on viscosity and rate of cure (*283*), and which was later presented by Bocquet (*40*) before a meeting of the International Organization for Standardization in October 1950.

Newton, Philpott, Fairfield-Smith, and Wren (*211*) made an extensive study of the variability of Malayan rubber as evidenced by Mooney viscosity and vulcanization characteristics, preparatory to the establishment of limits or boundaries for classifying the rubber on a technical basis. They found no technical justification in degrading smoked sheets, as is done under the present system, because of the presence of bubbles in the sheets.

Le Bras (*156*), Mann and Newton (*176, 206*), de Haan-Homans (*110*), Hublin (*127*), Heinisch (*117*), and others (*129, 164, 238*) have written good reviews, histories, descriptions, and comments on recent progress on the scheme for classifying and identifying crude natural rubber on the basis of viscosity and rate of cure. The International Rubber Research Board (*136*), in order to publicize the new types of classified rubber, began issuing two series of bulletins under the editorship of R. G. Newton, its Coordinating Officer for Technically Classified Rubber. One series, called the *News Sheet*, is distributed primarily to rubber dealers and manufacturers' buyers and executives to provide them with general information in a brief but informative manner about technically classified rubber. *News Sheet* No. 1 (*210*) was issued in February 1951.

The supplementary series, known as *Users' Information Circulars*, provides detailed technical information for the factory technologist. Its first issue (*208*) also appeared in February 1951. The second issue (*209*), released in October, summarizes results of some recent laboratory-scale evaluations of technically classified rubbers. Vulcanization characteristics change but slightly upon storage as compared with viscosity values. Some thought has been given to subjecting the rubber to a light mastication before viscosity measurement.

Whorlow (*302*) says that any attempt to check the correctness of grading a rubber for Mooney viscosity by means of the Williams instrument will lead only to confusion, since no correlation has been found between the results of the two instruments.

Arentzen and den Breejen (*9*) investigated the system of technical classification as used by the French rubber technologists, and modified their apparatus and procedures somewhat in order to make use of available material and also to bring the procedures more in line with those used in the American industry, where most of the rubber is processed.

In an evaluation of the vulcanization characteristics of rubber, Thirion (*288*) states that the usual stress measurements at 600% elongation give good discrimination between rubbers but do not always give sufficient indications of the vulcanization characteristics. He proposes to complete this evaluation by adding a second vulcanization corresponding to a different time of cure. Blow (*37*) and Fletcher (*95*), however, recommend the testing of three different cures by means of a strain tester under a low load, such as 10 kg. per sq. cm., in order to complete vulcanization characteristics. Thirion (*288*) also believes that the measurement of stress at low elongation would offer many advantages over that at 600%. Besides the viscosity test, Blow (*37*) also suggests that limits be set for the dirt content of the rubber. Analysis for dirt was discussed in section on Chemical Analysis.

McKeown and Williams (*171*) state that the packing specifications issued by the Rubber Manufacturers' Association (*241*), which became effective January 1, 1951, should be more specific. They are not sufficiently explicit to prevent certain undesirable practices frequently followed, such as the addition of excessive talc, inadequate identification marks, and objectionable bale coatings.

VULCANIZATES

STATIC TENSION AND COMPRESSION

An extensive general discussion was given by Usherwood (*292*) on the various types of tension test pieces: dumbbell, ring, and thread. As the sharpening of dies for cutting test specimens requires considerable experience, Taylor (*285*) developed fixtures to position the dies so that the surface to be ground may be held firmly in position, permitting operation by less experienced operators.

Baldwin-Lima-Hamilton Corp. (*16*) announced an improved low-cost Universal testing machine of 12,000 pounds' capacity, designated as model 12-H, which has many features of the larger Baldwin machine. The Instron Engineering Corp. (*135*) has added several new compression accessories to extend greatly the versatility of the Instron tensile tester.

Scott Testers, Inc. (*258*), announces that it is now manufacturing a strain tester that performs elongation measurements on rubbers in accordance with the method developed at the National Bureau of Standards. The method of selecting the loading weights has been greatly simplified over existing machines by mechanical rather than electrical operation. Four sets of weights, each set containing 18 weights, provide stresses of 50, 100, 200 or 400 pounds per square inch.

Dunlap, Glaser, and Nellen (*79*) use an inclined plane tester to determine the intrinsic low-stress properties of rubber compounds, which give better correlation between laboratory tests and tire performance than is possible with conventional testing. Data obtained by this technique provide an accurate measure of the rate of cure, the tendency to scorch, and the hysteresis loss. Dahlquist, Hendricks, and Taylor (*72*) use constant-stress elongation tests to determine the elasticity of soft polymers by means of a special apparatus. The constant stress is achieved by employing a tension weight in the shape of a hyperboloid. As the test specimen stretches, the weight is lowered into a liquid, and the buoyancy reduces the load in proportion to the decrease in cross-sectional area of the test specimen. The method has proved to be highly successful for characterizing unvulcanized polymers and for evaluating plasticizers in uncured compounds.

Boonstra (*44*) measured the stress-strain properties of natural rubber under biaxial strain. He obtained 600% axial and 300% tangential elongation simultaneously by stretching a tube-shaped sample in a direction parallel to the tube axis and at the same time inflating the tube to cause a tangential extension. Stresses were caluclated from the pressure in the tube and the dynamometer readings.

By using fixed pulleys and by lubricating the rubber test ring specimens with castor oil, Scott (*257*) obtained results for tensile strength and breaking elongation slightly higher than when using rotating pulleys in the conventional ring method.

Kruse (*152*) described in considerable detail experiments which he conducted on a micro scale to examine the stress-strain properties of a small sample under a low-power microscope. Munzinger (*202*) used a photocell in an optical method for recording the stress-strain curve, recording not only the stress-strain relation but also the speed at which the load increases.

The British Standards Institution (*51*) describes the methods that it recommends for the mixing and vulcanizing of rubber test compounds. The methods of mixing and vulcanizing, and the testing procedures, both physical and chemical, which have been used at the Netherlands Government Rubber Institute are described in a circular released by the Research Association for British Rubber Manufacturers (*234*).

Van Dalfsen (*73*) determined relationships between stress-strain and other mechanical properties of rubber vulcanized in a mercaptobenzothiazole mixture. He recommends the selection of a reference observation—e.g., the tensile stress at 700% elongation of a vulcanizate cured for 60 minutes at 127° C. in the ACS-I mix; and from this value, along with equations developed by the author, it is now possible to calculate the stress at other elongations, the tensile at break, the elongation at break, and the Shore hardness.

Shade (*248*) developed a method for using strain data as a basis of comparing cures of rubber compounds and selecting an optimum cure. Equations relating time of cure, T, and elongation of vulcanizates, E, under a fixed load make it possible to calculate the rate of change of elongation for any time of cure, dE/dT, and the corresponding acceleration of the rate of change, d^2E/dT^2. It is also possible to calculate the times of equivalent cures of different vulcanizates by means of equations which relate the time of cure to these two criteria.

Interlaboratory testing of tensile properties (*6*) gave agreement which was very good for measurements made by strain testing machines at constant load, only fair for measurements of stress at 600% elongation, and poor for measurements of ultimate tensile strength. Analysis of the data indicated that the large variation in breaking strength was probably caused by variations in technique in dieing out the dumbbell test specimens. Späth (*269*) stresses the idea that the tension at breaking point should be calculated from the cross section of the test specimen at the time of break, which can be obtained from the elongation. This value, he says, should be known as the tensile strength, and the term "tensile product" should be abandoned.

Mullins and Newton (*200*) studied the effect of previous stretching of dumbbell specimens on the tensile properties of the rubber. They used two test specimens in series for the first test, and the unbroken one for the second test. The conclusion was that the previous stretching had no visible effect on the tensile strength. Mullins (*196*) also studied the effect of previous stretching on other physical properties. Abrasion by the Du Pont machine was not affected. Neither was tear on a pure gum vulcanizate, but when the rubber was loaded with MPC black the tear strength was increased if the tear took place at right angles to the previous stretch. This increase was probably caused by orientation of the anisotropic filler structure in the direction of stretch. The increase of set in normal set tests associated with the presence of fillers in a rubber vulcanizate is also attributed (*198*) to an orientation of anisotropic filler particles. The use of set tests to assess the degree of vulcanization of loaded vulcanizates may therefore be misleading, and an alternative test procedure is suggested (*199*).

Dogadkin and Gul (*75, 76*) designed an apparatus which enabled them to study the effect of swelling of an elastomer on its deformation characteristics. Ring-shaped test specimens can be stretched or compressed by weights in a thermostat into which vapors of the desired solvent are introduced along with nitrogen gas. Data may be obtained on deformation and on relaxation of stress after swelling. Boström (*48*) describes a new apparatus for measuring the relaxation of elastomers. He uses dumbbell-shaped test specimens and measures the stress relaxation at a given elongation by means of a dynamometer.

Farnam (*91*) developed an apparatus for determining relaxation at room temperature and at elevated temperatures. Results from test in this apparatus are indicative of the behavior of gasket material of various types. The American Society for Testing Materials (*4*) introduced a tentative test, D 1147-51T, for determining the compressibility and recovery of gasket materials. Greenleaf (*108*) describes properties which a gasket material should possess in order to be suitable for sealing doors, ports, and hatches aboard naval vessels used in Arctic service.

HARDNESS

In a series of articles written by Soden (*264*) the whole field of hardness of rubber is surveyed in considerable detail. The theoretical aspects of the subject are discussed, and the various standard hardness tests are explained. The author then deals with the factors affecting the design and use of hardness testing instruments and their calibration. A large bibliography of references is included in the paper, together with appendixes giving hardness conversion values for the different tests. This series of articles was later reprinted in the form of a book (*266*). In another article Soden (*265*) describes the derivation of the scale of British standard hardness degrees, and gives a correlation between this scale and that for Shore hardness.

Scott (*256*) discusses the common sources of error in hardness testing and the recent improvements made in increasing the accuracy. The application of a gentle vibration to the instrument gives more consistent readings because of reduced friction. Lubrication of the surface of the test piece with talc also produces a further improvement in the uniformity of results. In another article (*255*) the same author describes an indentation test conducted on ebonite at elevated temperatures which measures essentially the same physical characteristics as does the torsion plastic-yield test. The measurement can be made conveniently by an ordinary dead-load hardness gage.

ABRASION

Abrasion tests still fail to give satisfactory correlation with actual practice. Newton (*205*) compared nominally identical abrasive wheels on Akron abraders in different laboratories and found that the abrasive loss varied considerably. Burns and Storey (*65*) were able to obtain better correlation between laboratory abrasive testers and actual practice when they replaced the usual abrasive paper of the National Bureau of Standards abrader by a steel screen. The Taber Instrument Corp. (*284*) announces an improved model of the Taber abrader which is sturdier than the previous model.

Kendall and Moakes (*141*) measured abrasion resistance of vulcanizates both before stretching and after they had been stretched close to the breaking elongation, and could find no appreciable effect of the stretching on the abrasion as conducted by the Du Pont and the Akron machines.

Adams, Reynolds, Messer, and Howland (*1*) undertook the evaluation of several abrasion machines, and decided that the Lambourn (Dunlop Rubber, Ltd., England) was the most promising for the evaluation of new elastomers and carbon blacks for tire treads. Buist, Newton, and Thornley (*59*) developed a technique involving modern statistical methods to distinguish between effects that are due to real differences between the compounds and effects of various extraneous factors in the test. Buist (*57*) believes that most laboratory machines operate under conditions too severe for good correlation with actual practice. He presents a mathematical equation which is said to be applicable to wear data on various laboratory abrasion machines. The data can be used to estimate road service.

Stiehler, Steel, and Mandel (*174, 276*) studied the tread wear of tires by measurement of both the tire weights and the depths of the tread grooves. The advantages and disadvantages of each method are presented, together with an analysis of the precision of road tests. The road tests were designed statistically to evaluate brands of tires, types of rubber, types of carbon black, wheel positions, seasonal variations, and weather conditions. Stechert and Bolt (*274*) developed a method for evaluating tire wear based on either the loss in nonskid depth at an arbitrary mileage or a definite percentage of nonskid loss. Extrapolation is then made to the mileage of tire baldness.

Recent research at the laboratories of the British Rubber Producers' Research Association (*50*) led to the conclusion that the hardness of the tread compound is important only in that it limits the movement of the tire on the road. The actual wearing surface is softened by the working to which it is subjected. Späth (*270*) reviewed and discussed the measurement and interpretation of abrasion of rubber, and made special reference to the recent work of Buist.

ADHESION

Borroff, Elliott, and Wake (*46*) studied the effect of stripping rubber on the measured adhesion between plies of conveyor belting, and found that although the ply adhesion is dependent on the rate of stripping, the rate can be varied from 0.2 to 5 inches per minute without seriously affecting the results because of the large experimental error. The strength of a rubber-to-fabric bond is a simple function of the number of fibers ruptured in breaking the adhesive bond and the strength of the individual fibers (*47*).

Lyons (*168*) developed a practical and reasonably rapid method for evaluating the resistance of the adhesive bond between the tire cord and rubber stock to flexural (dynamic) fatigue. The test cords, cured in rubber and under tension, are subjected to rapid cyclic flexure by being passed back and forth around small steel rollers. After flexing, the resistance of the adhesive bond to fatigue is evaluated by measuring the cord adhesion by the familiar H pull-out test. Dynamic adhesion measurements by this method have been found to correlate reasonably well with the adhesive performance in road tire tests.

Methods used at the R. T. Vanderbilt Co. laboratories for testing adhesion in rubber-to-metal bonding (*295*) include the ASTM method, 180° shear test, 90° shear test, and slip-off adhesion test, often used for wires. A panel discussion on rubber-to-metal bonding contains a section on molding and testing by French (*99*). Buist and coworkers (*58*) believe the conventional methods of testing bonded strength are unsatisfactory, and describe a new and better procedure of evaluation in which the bonded unit is tested by impact of a falling weight. This test not only gives better evaluation of metal-to-rubber bonding agents but also leads to a better understanding of the facts underlying the design of rubber-metal spring units. Kaercher and Blum (*138*) developed a test method for measuring the bond strength between Butyl rubber and brass. The test is based on the pull in pounds per square inch, normal to the plane of bonding, which is required to rupture the bond. Malden (*173*) applied the technique of electron diffraction to problems of bonding.

Moakes (*189*), after visiting with American technologists, described the tests used in various laboratories of the United States for evaluating the adhesion of rubber to fabrics.

Parris (*222*) reviewed the methods used in testing the adhesiveness of insulating tapes, and describes and criticizes a number of them. Voet and Geffken (*296, 297*) considered the fundamentals of tackiness, and designed an apparatus which permits the measurement of energy of film separation under dynamic conditions by the energy loss of a cylinder rolling over an adhesive film. Saint-Mleux (*245*) devised a method for measuring the adhesion coefficient and the factor of safety of latex adhesives. Parts of surfaces of each of two pieces of rubber are roughened, coated with the adhesive, dried, and then stuck together under pressure for 24 hours. The adhesion is then measured by separating the halves perpendicular to the plane of adhesion.

Bachman and coworkers (*14*) describe the determination of a "sticking point" of a rubber, which they define as the temperature at which the polymer softens sufficiently to stick to a bar. This test does not coincide with the softening point. Bekk (*24*) describes what seems to be a similar property and stresses the importance of a test for this sticking point in evaluating material to be used for gaskets, or where friction is a factor.

Schricker (*252*) describes an apparatus which provides sealing conditions for adhesives and then determines the strength of the heat-sealing seams.

ELECTRICAL PROPERTIES

Waring (*300*) measured the electrical power factor of rubber over a wide range of curing systems, and found that although the power factor increases as the combination of sulfur increases, no simple conversion factor could be obtained to change power factor into quantity of combined sulfur. This indicates that the electrical losses are affected by the type of sulfur combination. Schallamach (*249*) measured electrical properties of natural rubber vulcanizates as a function of frequency, and concluded that the dielectric loss is mostly due to the sulfur which has been combined in forms other than cross links because the losses in vulcanizates containing the same amount of sulfur decrease with increasing modulus. The structure of vulcanizates was also studied by Thirion and Chasset (*289*) by applying measurements of dielectric constant and loss angle.

Hand and Winans (*113*) describe in detail the construction of equipment they used for measuring dielectric strength of insulating materials at temperatures up to 250° C. Mullins (*197*) determined the electrical breakdown strength of rubber when surrounded by different media, and showed that differences of more than 30% may be obtained for a given material between tests made in air and in standard transformer oil. Parry (*223*) describes a resonance method for measuring permittivity and power factor of dielectrics at frequencies from 300 to 600 Mc. per second.

Sperberg, Popp, and Baird (*271*) describe a method which they used to measure the electrical resistivity of various carbon blacks in natural and synthetic rubbers in order to study the effect of the type of carbon black, type of rubber, state of dispersion of the carbon black, and flexing on the electrical resistivity of vulcanizates containing various carbon blacks. McKinney and Roth (*172*) modified ASTM method D 991-48T (*4*) to measure electrical resistivity of vulcanizates and concluded that it is possible to use resistivity to supplement tensile data for differentiating between different types of carbon blacks and for detecting variations between lots of the same type. Norman (*214*) studied contact resistance of various electrodes for testing electrically conductive rubber. He found that brass attached to the specimen by vulcanization never gave a measurable contact resistance. In an already vulcanized rubber he recommends the use of tin foil attached to the sample by colloidal graphite.

Havenhill and coworkers (*116*) describe electrical test equipment for evaluating rubber and associated materials. They found that electric charges are specific for each ingredient, and by means of an electric charge recorder they can follow the breakdown of the rubber, the state of incorporation of pigments, oils, and other ingredients during mixing in an internal mixer without disturbing the operation. Hurry, Bolt, and French (*128*) state that the electrical conductivity alone is not an adequate criterion of the ability of a rubber product to dissipate an electrostatic charge. They developed a method which measures the ability of a vulcanizate to "bleed off" self-generated or imposed electrostatic voltage.

DYNAMIC PROPERTIES

At the September 1951 meeting of the AMERICAN CHEMICAL SOCIETY the Division of Rubber Chemistry held a Symposium on Dynamic Properties of Rubberlike Materials, at which six papers were presented (*8*, *68*, *92*, *109*, *181*, *184*), all of which are referred to later in this section. Marvin (*181*) reviewed the present status of dynamic testing, described the various methods used, and predicted that with the recent advances in the techniques of making dynamic measurements and with the improved understanding of the effects of frequency and temperature, the next few years should see great applications of dynamic measurements both to determine the effects of structure on mechanical behavior and to aid in the testing of rubber stocks and products. Späth (*268*) believes that the great rivalry between natural and synthetic rubbers will cause an increased trend toward the measurement of energy dissipation in elastomers. Haushalter (*115*) emphasizes the need for more critical requirements for automotive rubber parts, such as those for dynamic modulus and resilience of compounds used for motor mounts.

Enabnit and Gehman (*85*) describe measurements of dynamic properties on raw and vulcanized elastomers. Their data show that a definite correlation exists between the properties of raw elastomers and those of the same elastomers after vulcanization. The effect is the same for a loaded raw elastomer as for the loaded vulcanizate. It should therefore be possible to predict from measurements of raw elastomers the dynamic properties of the vulcanizate. Andrews (*8*) was able to find fair correlation between certain dynamic properties and static properties. Waring (*299*) measured both dynamic moduli and electrical conductivity on the same tread stocks at a series of temperatures. He found a change of conductivity with temperature and also with amplitude of vibration (sample undergoing vibration while conductivity measurement was made), and presents some speculations as to the meaning of his results in terms of carbon-to-carbon, rubber-to-rubber, and rubber-to-carbon bond structures existing in the stock.

Rorden and Grieco (*236*) and also Hopkins (*126*) investigated the dynamic properties of rubberlike materials over a wide range of frequencies, employing both a horizontal pendulum method and a tuning-fork method. The precision of the tuning-fork method was not very high, but its simplicity and its large frequency range recommend it for exploratory measurements. Morris, James, and Snyder (*193*) employed a piezoelectric transducer to generate vibrations at various frequencies in the audio range, and used an identical one as a detector. Samples of rubber compressed to 20% deflection between the faces of the two transducers were measured for transmission of mechanical vibration for the purpose of studying rubbers suitable for mountings. Gui, Wilkinson, and Gehman (*109*) found nonlinear vibration characteristics in tread stocks in the mechanical range of frequencies, which appear to be sufficiently large to be taken into account in any exact studies of the modulus on tread wear and performance.

Ferry and coworkers (*92*) reviewed the reduced variables by which dynamic measurements made at different frequencies and temperatures can be shown on a single plot, and discussed the derivation of a distribution function for relaxation times. Isakovich (*137*) employed an impulse-phase method for determining the mechanical parameters of rubbers. The test method is described in which the sample is immersed in water in an impulse tube in which are set up short wave trains of acoustic waves, and the shear modulus of the sample is found from the wave modulus.

Cathers, Bailey, Buchy, and Asness (*68*) employed high-frequency ultrasonics in a study of high polymeric materials to obtain information concerning the liquid state of the elastomers. A comparison was thus made of the ultrasonic behavior with the second-order transition temperatures of the butadiene-styrene polymer system. An improvement in experimental technique was introduced by Melchor, Petrauskas, and Guth (*184*) for the measurement of velocity and attenuation of ultrasonic sound in rubberlike materials which permits a precision of about 0.03% in the determination of the velocity of sound. They also extended ranges of conditions such as temperature and frequency, but aimed chiefly at the high degree of precision, so as to observe possible breaks at the second-order transition temperature for the curve of the velocity of sound versus temperature. Hatfield (*114*) describes the measurement of velocity and the absorption coefficient of low-amplitude ultrasonic waves in rubbers.

Martinon (*180*) designed an apparatus to measure internal friction, independent of other mechanical properties, with which dynamic hysteresis cycles of vulcanizates under compression are recorded on paper by an optical system. The principle is similar to that of the Roelig oscillograph, but the apparatus is smaller and more easily operated. Painter (*219*) measured the dynamic modulus of elastomers by a vector subtraction method in which he employed a device for measuring real and imaginary parts of the complex modulus, comparing the amplitude of vibration and the force transmitted through the sample as in the Roelig machine but utilizing strain gages for measuring stress and strain. Goudy and Hobley (*106*) redesigned the Roelig machine in their study of dynamic hysteresis and fatigue testing of rubber. The new machine now can handle specimens up to 8 inches in tension, compression, or shear at frequencies up to 1500 cycles per minute and at temperatures between −40° and +150° C.

Nielsen, Buchdahl, and Claver (*212*) measured shear modulus and damping of polymers at different temperatures by means of a new design of recording torsion pendulum for their study of molecular structure and transitions of rubberlike materials. Lethersich (*160*) describes an apparatus to study the creep of dielectric polymers based on their dynamic rheological properties. Shear stress is applied rapidly to solid materials and the strain is measured a few milliseconds later. The apparatus can also measure dynamic modulus and internal friction. Piganiol (*228*) describes an apparatus which can be used to determine the mechanical properties of materials such as ebonite over a wide range of frequency and temperature.

Gardner and Worswick (*100*) studied the behavior of tires at high speeds, and noticed that as the speed of a tire running under load against a circular drum is increased, stationary waves make their appearance around the circumference of the tire. The amplitude and persistence of the waves increase with increasing load and with decreasing inflation pressure, and are also affected by the tread weight and by the stiffness of the casing.

LOW-TEMPERATURE TESTING

Pollack, Emmett, and Cobbe (*229*) describe a low-temperature flexibility tester which operates over a wide range of temperature, accommodates a number of samples at the same time, provides no contact between the samples and the liquid bath, and avoids handling or mechanical factors. From the curves obtained by plotting the deflection against temperature, the authors recommend that three criteria be determined and used to evaluate low temperature performance: stiffness temperature, rigid temperature, and stiffening rate.

Smith, Hermonat, Haxo, and Meyer (*263*) describe a retraction test employing large deformations, based on the familiar T-50 test, which can measure the merits of a rubber for low-temperature applications. The large deformations greatly accelerate crystallization and consequent stiffening, and therefore decrease the time necessary to conduct the test. Good correlation is obtained between this test and the ultimate stiffness of vulcanizates at low temperatures. Svetlik and Sperberg (*282*) elaborated the original T-50 test into a more general test, which they call the T-R (temperature-retraction) test, by including temperatures corresponding to a large number of retractions after different elongations rather than just the one temperature corresponding to 50% retraction. The authors claim a complete characterization of the properties of an elastomer in a shorter time than by any other test method or combination of methods. The test is simple to perform, highly reproducible, and very versatile.

Wolstenholme and Mooney (*306*) measured the modulus and relaxation of elastomers in torsion in order to evaluate the characteristics of elastomers at low temperatures. Rods of gum vulcanizates were held twisted at low temperatures, and the torque was measured over time periods extending to 5 months or more. Crystallization of the rubber was found to depress the torque, and lower modulus values were observed as temperatures approached that of the second-order transition. Nielsen, Pollard, and McIntyre (*213*) also studied transition temperatures of polymers by means of torsional apparatus. A second-order transition takes place where the modulus-temperature curve has an inflection point. The authors used this technique to study the effect of plasticizers on copolymer systems, and concluded that the transition temperatures of the plasticized compositions can be predicted from the transition temperatures of the pure polymer and pure plasticizer, and also that the transition temperatures of homogeneous copolymers can be predicted from the transition temperatures of the individual polymerized monomers making up the copolymer. Boyer (*49*) shows that a linear relationship does not always exist between the tensile strength and transition temperature for plasticized polymers independent of the nature of the polymer, and suggests that the diffusion rate of a plasticizer molecule is important in the fast brittle-point test.

Lichtman and Chatten (*161*) indicate the feasibility of the use of either the stiffness test, as measured by flexural or torsional deformation instruments, or the hardness test, as measured by indentometers, to evaluate the properties of elastomers at low temperatures.

Labbe (*154*) conducted tests on five different available grades of torsion wires for the Gehman apparatus used for the determination of low-temperature stiffness of elastomers. The ASTM specification D 1053-49T (*4*) is vague, in that it specifies thickness and length of wire rather than torsional constant. Labbe recommends as the best wire for use, one which has a torsional constant of about 0.500 gram-cm. per degree of twist. If, however, the twist is more than 170° or less than 120° at 25° C., other wires are recommended.

Morris, Hollister, and Shaw (*192*) found that the cold compression set performed at −35° F., gave good indication of the performance of a rubber as a gasket material to be subjected to low temperature service. This test was also used successfully (*191*) to evaluate plasticizers for GR-S rubber gasket stocks to be used at low temperatures.

As low temperature performance is associated with the structure of the molecules and their transition points, it is recommended that the reader refer to the section on Molecular Structure for further information along this line.

MISCELLANEOUS

Boonstra (*45*) developed a simple method for the determination of the dynamic coefficient of friction of vulcanized rubber, in which molded rubber wheels are pulled over a piece of road-like material. The wheels are forced to rotate with a speed non-concordant with the linear speed on the surface, so that friction occurs which is measured by a dynamometer. Giles and Sabey (*102*) in connection with experiments to test the skidding resistance of tires on roads, developed a method utilizing photographic film wrapped in light-tight envelopes to study the pressures and friction between tires and the peaks of projection in road surfaces.

A special technique was developed and described by Cooper (*69*) which determines stiffness and creep in vulcanized rubbers containing various proportions of carbon black under constant load at 70° C., with the view of predicting more accurately the deflection of rubber springs. Meyer, van der Wyk, and Gonon (*187*) described a novel apparatus for the study of mechanical behavior of cylindrical specimens of rubber at very small torsions. Blevins and DeFries (*36*) present a nomogram which expedites the calculation of stiffness in flexure and precludes the necessity of plotting a curve and measuring its slope.

Lippman and Ferguson (*163*) developed a tire tread noise analyzer which employs an electronic system to analyze the noise signal developed by a tire rotating against a drum. The Avon India Rubber Co. (*12*) describes a machine developed for measuring the power consumption of a tire. Provision is made for controlled variation of speed, inflation pressure, tire load, slip angle, and driving and braking torques. Capacity of the machine is 50 hp., wheels are up to 33 inches in diameter, and road speeds are from 30 to 120 miles per hour.

Dauphinee, Ivey, and Smith (*74*) describe an apparatus which they use to determine the thermal conductivity of elastomers at elongations of from 0 to 100% and to temperatures from +50° down to −170° C.

Stambaugh (*272*) devised an electrical analog for explaining the behavior of elastomers. Typical models are described, one of which produces data illustrating in a fraction of a second the creep which takes place in an actual rubber stock over a period of 1000 hours.

Endres, Coleman, Pierson, and Sinclair (*86*) developed tests to show the ability of a mixture of rubber powder in asphalt to withstand repeated impacts without undergoing excessive plastic flow. This test is believed to simulate road conditions where high loads are applied for a short time and removed for longer periods.

Best (*28*) describes the apparatus and methods which he used for the determination of the diffusion coefficient of waxes through rubber.

The Ferry Machine Co. (*93*) announced the production of a foam latex compression-indentation tester, which measures the load necessary to produce a 25% indentation in a test sample.

The Rubber Manufacturers' Association, in cooperation with the American Hospital Association (*240*), specified minimum requirements which they recommend for latex foam mattresses to be used in hospitals. Methods of testing are also included.

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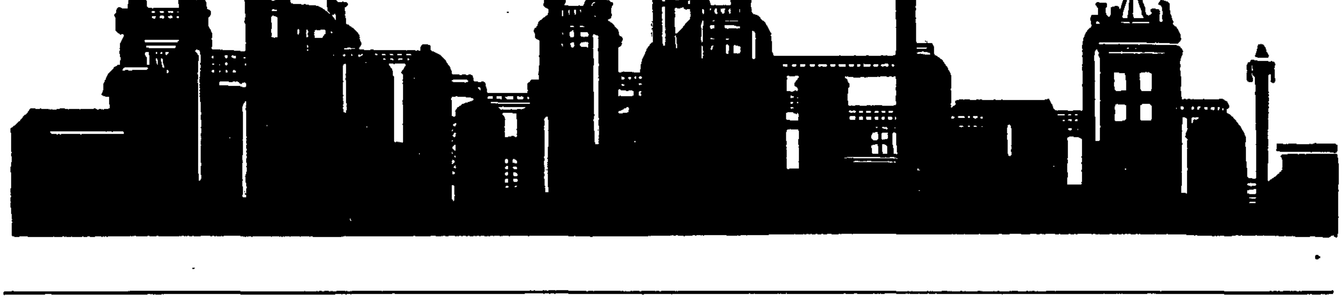

WATER ANALYSIS

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THIS is the fourth annual review of analytical procedures applied to the analysis of water and reported in the technical literature. Previous reviews were published in 1949 (*68*), 1950 (*69*), and 1951 (*70*). In each annual survey mention has been made of outstanding developments and increasing use of instruments in water analysis. In this review a separate section is devoted to instrumentation. Another section is given over to the qualitative detection of trace elements in water, and a third discusses advances in colorimetry applicable to water analysis.

Of great usefulness to analytical chemistry the world over will be the book "Reagent Chemicals" (*18*) published in 1950 by the AMERICAN CHEMICAL SOCIETY. This book, which is the culmination of a tremendous amount of work covering nearly half a century, lists recommended limits of impurities and methods of testing for 177 reagent chemicals. No up-to-date analytical laboratory can afford to be without it.

INSTRUMENTATION

Several papers on the general aspects of flame photometry have appeared in the literature. Dunker and Passow (*23*) discuss the requirements of an instrument for best accuracy. They recommend high gas pressure and a very fine spray. An important point, sometimes overlooked, is the necessity for identical physical properties (surface tension, viscosity, temperature, etc.) in the sample and standard. Their discussion of effects of stray radiation is more pertinent to instruments using filters to isolate the wave-length spectrum than to the flame spectrophotometers now generally in use. Heidel and Fassel (*41*) describe an internal standard flame photometer built around a Gaertner constant-deviation monochromator. Two photomultiplier tubes are used in a balanced bridge circuit. The instrument features a unique "recycling" atomizer which provides that only the fine spray droplets enter the burner and provides recovery of the condensate of large drops, which usually runs to waste, and recycles this condensate through the atomizer. Following the trend toward internal standard instruments, Fox (*29*) describes a filter-type instrument using two barrier-layer cells in a balanced bridge circuit. He uses a centrifugal principle to provide a fine, dry aerosol which is fed to a Meker-type burner. Excellent reproducibility is claimed using propane or city gas. The instrument was used for the determination of sodium and potassium and is probably limited to these elements because of the lack of electronic amplification.

The subject of operation of flame photometers for best performance was thoroughly discussed at a round-table meeting of the Division of Analytical Chemistry of the AMERICAN CHEMICAL SOCIETY. A digest of the discussion with W. G. Schrenk (*114*) as moderator outlined the essentially practical aspects of analysis by flame photometry.

Rayner and Logie (*107*) describe an apparatus that determines the solids in steam condensate automatically. Large samples of water are evaporated in a platinum pan attached to one arm of a balance. The other arm carries a counterpoise weight and frictionless mercury contact which operates electrical circuits to control the amount of sample delivered to the pan.

A portable meter for determining dissolved oxygen is discussed by March (*76*).

Automatic equipment for recording residual chlorine in water is described by Hazey (*38*).

Antimony electrodes are used in a modified continuous recording pH meter described by Kordatzki (*53*).

Love (*71*) has presented a review of analytical instruments used in water plant laboratories.

A continuous odor monitor and threshold tester was developed by Gerstein (*31*). The sample is fed continuously through a rotameter flowmeter, heated to 140° F., and sprayed into a bell jar where the operator determines odor using a standard glass osmoscopic nosepiece.

Kline (*50*) describes an automatic sampler for certain industrial wastes. Compressed air is used to operate the apparatus, which takes samples at 10-minute intervals, and composites them for 24 hourly samples by means of a turntable distributor.

TRACE ELEMENTS

The water chemist is often called upon to provide information about trace elements in water. To make expensive quantitative determinations of a large number of elements that are seldom present in determinable concentrations would require more time and effort than ordinarily can be justified. Frequently chromatographic or spot tests can be made to indicate the presence or absence of specific trace elements. Quantitative tests can thus be reserved for those elements shown to be present in significant amounts.

A paper by Lederer (*66*) which gives reference to earlier publications essential to the use of his methods, covers the paper chromatographic identification of a large number of trace elements. The chromatograms are developed with hydrogen sulfide, ammoniacal alizarin, azoresorcinol, ferrocyanide, dipicrylamine, hydrogen peroxide, and ammonium rhodizonate. Many of the tests are of sufficient sensitivity for use with natural waters without concentration, but some—strontium and barium, for example—would require concentrated samples for sufficient sensitivity.

Another complete study of metallic ion identification by means of paper chromatography is given by Pollard, McOrmie, and Elbeih (*98*). In addition to most of the metallic ions, a scheme is given for anion analysis including the common anions and many trace anions such as arsenate and chromate. Lacourt and coworkers (*59*) give a chromatographic scheme which is concerned essentially with the more common elements.

Oedekerken in two papers (*90, 91*) presents a semimicro and spot test qualitative scheme based on the use of specific organic reagents for the identification of the more common anions and cations. Most of the tests are sufficiently sensitive for water analysis and employ accepted reagents—for example, dimethylglyoxime for nickel, Titan yellow for magnesium, etc.

Hovorka and Diviš (*48*) report spot tests for mercury (red), copper (brown), and cobalt (green) using 2-isotoxime. Prodinger and Kral (*105*) studied three well-known tests, the detection of manganese with Arnold's reagent, the detection of copper with benzidine and iodide, and the detection of cobalt with pyridine and thiocyanate. New and very sensitive reagents for halides are reported by Kuznetsov (*57*). Silver ion forms a pink complex with 4-(8-hydroxy-5-quinylazo)-benzenesulfonic acid which turns yellow in the presence of agents that precipitate or complex silver (halides, thiocyanate, sulfide, thiosulfate, nitrilotriacetate). The reagent is sensitive to 1 microgram of bromide or 0.5 microgram of iodide. Three other dyes which may be used in the form of the silver or mercury complexes are described and chloride, bromide, and iodide sensitivities are given.

A general review of spot test analysis is presented by Feigl and West (*26*).

APPLICATIONS OF COLORIMETRY

A series of papers by Hiskey, Young, and Rabinowitz (*43, 44*) outlines the principles of high precision colorimetry and the application to analytical problems. Comparison of a sample against a standard at high absorbance values permits accuracy equal to the best gravimetric determinations if the absorbance difference between sample and standard is made sufficiently small. Very careful attention to deviations from the absorption law must be observed, however. The principles are demonstrated in the determinations of manganese as permanganate (*134*). It is seldom necessary to make use of the full accuracy of which the method is capable in water analysis at present, but in view of the rapid adoption of colorimetric methods and their rapid refinement, it may be anticipated that they will some time receive general use at the higher concentrations now reserved for volumetric and gravimetric methods. In such cases it will be necessary to make measurements with all possible precision.

Berger and Verbestel (*6*) give a general discussion of colorimetric methods in water analysis, including the fundamentals of light absorption and the performance characteristics of several types of photelectric instruments.

A complete outline for the colorimetric determination of trace metals in sewage and industrial wastes using the Beckman DU spectrophotometer is given by Butts, Gahler, and Mellon (*15*), who recommend the following determinations with the reagents at the wave lengths indicated.

		mμ
Cadmium	Dithizone	510
Chromium	Diphenylcarbazide	540
Copper	Diethylhydroxydithiocarbamate	435
	2,2′-Biquinoline	545
Iron	1,10-Phenanthroline	508
Lead	Dithizone	520
Manganese	Permanganate	445
Zinc	Dithizone	535

The universal complexing action of ethylenediaminetetraacetic acid and its salts as described in the publications of Schwarzenbach and coworkers is extending the use of the complexing agents beyond the field of calcium and magnesium titration, where their place has been firmly established. Přibil and coworkers, in a series of publications (*101–104*) are reporting on the use of ethylenediaminetetraacetic acid salts in metallic ion analysis as both complexing agent and colorimetric agent. The problem of complexing the fluoride ion which interferes in several colorimetric determinations made in natural water was attacked by Feigl and Schaeffer (*25*), who used beryllium nitrate as demasking agent for fluoride. The extremely stable boron tetrafluoride anion is formed.

IRON, ALUMINUM, AND BERYLLIUM

A significant study of iron determinations was reported by Reitz, O'Brien, and Davis (*108*), who studied the effects of variables in three colorimetric iron methods, the 1,10-phenanthroline method, the thiocyanate method, and the sulfide method, by means of a factorially designed experiment. This method permits the statistical study of the effect of interactions of several variables as well as the effect of variation of a single condition. The 1,10-phenanthroline method was found superior on all counts. The study is of interest not so much for its information about three already thoroughly studied iron determinations as for its example of experimental design. Such a factorial design would seem to have many possibilities for the laboratory that deals with a wide range of natural water types and must take account of many variables in the design of its methods.

Wells (*131*) describes a potentiometric titration of iron in low concentration, which may be of value when better accuracy is desired than is afforded by the colorimetric methods. Haniset and coworkers (*37*) report on the determination of iron with pyrocatechol. An adaptation of the "ferron" iron determination to the Lange colorimeter is described by Haniset (*36*).

Two papers report on the color-intensifying effect of calcium in the alizarin red S determination of aluminum. Parke and Goddard (*95*) take advantage of the effect in a procedure for low aluminum concentrations. Back and Raggio (*2*) report similar findings, but also point out that calcium enhances the interferences of iron in the alizarin determination. Kul'berg and Mustafin (*55*) studied a series of hydroxy derivatives of anthraquinones as aluminum reagents. They appear to be highly specific and extremely sensitive. They serve as both colorimetric and fluorometric reagents, with generally better sensitivity in the latter capacity. A typical member of the group is 1,4-dihydroxy-5,8-dichloroanthraquinone, which gives a pink color and a yellow-green fluorescence with aluminum. Limits of detection are 0.5 microgram colorimetrically and 0.1 microgram by fluorescence. Rolfe, Russell, and Wilkinson (*110*) report on a study of Chenery's method of determination with ammonium aurin tricarboxylate using thioglycolic acid as iron reducing and complexing agent. The method is sensitive to 0.3 microgram. Teicher and Gordon (*126*) describe a separation of iron and aluminum using anion exchange resin saturated with ammonium thiocyanate. Iron is absorbed on the column as the negatively charged thiocyanate complex. Aluminum is washed out with ammonium thiocyanate at pH 1.0. At higher pH values recovery of aluminum is incomplete. Good separation requires careful control of conditions.

Furuhata (*30*) reports a new colorimetric reagent for beryllium. Details of procedure are given for colorimetric determination with disodium 3-(5-chloro-2-hydroxyphenylazo)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid. There is no fading with this dye as with quinalizarin. The author also recommends turmeric as a qualitative spot test for beryllium. In presence of oxalic acid the development of the characteristic red color suffers little interference from metals.

COPPER AND ZINC

Šedivec and Vašák (*117*) studied the use of ethylenediaminetetraacetic acid in eliminating the interference encountered in the determination of copper with diethyldithiocarbamate. Interference of iron, cobalt, nickel, and manganese is completely eliminated. Silver and bismuth give the customary yellow color, but these metals are rarely encountered in water analysis. LaCoste, Earing, and Wiberley (*58*) studied the extraction of diethylthiocarbamates and concluded extraction was an unsatisfactory method of removing interferences. Hoste, Heeremans, and Gillis (*46*) studied the determination of copper with 2,2′-biquinoline (cuproine) and reported a sensitivity of 0.02 microgram. Extraction is necessary.

Okáč and Čelechovský (*92*) studied the determination of copper with six organic reagents, antipyrine and potassium thiocyanate, phenolphthalein, benzidine, and potassium bromide, 1,2-diaminoanthraquinone—3-sulfonic acid, diphenycarbohydrazide, and 2 nitroso-1-naphthol-4-sulfonic acid. Interferences are discussed. Polster (*99*) describes a spot test adaptation of the Baudisch-Rothschild test using *o*-nitrosophenol. Nickel, cobalt, bismuth, and iron give small positive interference. The reagent must be prepared with care. Detailed instructions are given.

Belcher, Nutten, and Stephen (*5*) describe a new spot test for zinc using potassium ferricyanide and naphthidine hydrochloride or 3,3′-dimethylnaphthidine hydrochloride. The latter reagent has a hundredfold advantage in sensitivity. Some oxidizing agents interfere. Bertiaux (*7*) gives a nephelometric determination of zinc based on the precipitation with oxine in solution buffered with carbonate. Conditions must be standardized and sample should contain only zinc, ammonium ions, and alkaline earths. Morita (*83*) reports on a survey of copper and zinc content of sea water near Japan. An improved dithizone procedure was used.

CALCIUM, MAGNESIUM, AND STRONTIUM

The titration of hardness with sodium salts of the complexones, introduced by Schwarzenbach, has been almost exclusively performed using calcium and magnesium indicators for the detection of the end point, though it is pointed out by Schwarzenbach that considerable change in pH takes place in the end-point region. Hahn (*35*) has made use of this principle in the titration of calcium and magnesium with a mixture of ternary and quaternary salts of ethylenediaminetetraacetic acid, using pH indicators and potentiometric measurements for the detection of the end point. With indicators the titration is accurate to 0.5 mg. of calcium carbonate and with potentiometric measurement it is accurate to 0.1 mg.

Ostertag and Rinck (*94*) report the colorimetric determination of calcium with murexide. Magnesium reduces the sensitivity of the color up to a magnesium to calcium ratio of 40, at which point the effect levels off. LePeintre (*67*) reports a modification of the chloroanilic acid method of Gammon and Forbes. Okáč and Pech (*93*) report the use of pyrogallolcarboxylic acid as a colorimetric reagent for the alkaline earths, and Pech (*96*) describes a detailed procedure for the quantitative estimation of calcium. The sensitivity reported is satisfactory for determination of calcium in most natural waters. Lur'e and Nikolaeva (*73*) report a determination of calcium based on precipitation as calcium potassium nickel nitrite with subsequent colorimetric determination of the nitrite or nickel. The determination appears too complicated and susceptible to error for competition with the well-established Schwarzenbach method and its modifications.

Rozenberg (*111*) investigated the precipitation of calcium in natural waters by *Bacterium precipitatum*. His finding that up to 17% of the calcium in concentrations as high as 250 p.p.m. can be precipitated by the bacteria emphasizes a point that has received little consideration in studies of the preservation of natural water samples. The presence of carbon dioxide reduces the effect of the bacteria.

Shashkin (*118*) describes a new colorimetric reagent for magnesium, 1-amino-2-naphthol-6-sulfonic acid. The sensitivity is 1 part in 40,000. Copper, manganese, and high concentrations of iron interfere.

Smales (*122*) reports on a combined flame photometric and radiometric study of the determination of strontium in sea water. The extent of strontium coprecipitation in barium sulfate precipitates was determined by adding strontium 89 to the sample and determining the activity of the barium sulfate brought down. Another method involved determination of the original strontium concentration of the sample by flame photometry, and then after precipitation of barium sulfate, addition of standard strontium solution in known amount to restore the original level of strontium radiation intensity. Both methods gave similar results. In six samples of sea water 9 to 11 p.p.m. of strontium were found. Previously accepted values were 13 to 13.5 p.p.m.

SODIUM, POTASSIUM, AND LITHIUM

Although most water laboratories that make a practice of determining alkali metals now use the flame photometer, results of research on the conventional methods will be of interest to laboratories not so equipped.

Belcher and Nutten (*4*) describe an alkalimetric determination of sodium as the triple acetate. Potentiometric titration of the triple acetate and indicator titration are described. Using a mixed indicator, phenolphthalein and bromothymol blue, a range of 1 to 8 mg. of sodium can be covered. With potentiometric titration the range can be extended to 20 mg. and the accuracy is improved.

The cobaltinitrite determination of potassium has received considerable study with apparently no conclusive results. Belcher and Nutten (*3*) report inability to obtain good results with Wilcox's method involving precipitation with solution of trisodium cobaltinitrite, and prefer the reagent prepared with separate solutions of cobaltous acetate and sodium nitrite. Studies with x-ray show more uniform composition of precipitate with the latter reagent. Mason (*78*), on the other hand, prefers precipitation with a suspension of trisodium cobaltinitrite in ethyl alcohol. Bourdon (*10*) reports the cobaltinitrite precipitate to be lower than theoretical in potassium and higher in sodium. The author states 3% as average variation in results. Kriventsov (*54*) presents a review of the cobaltinitrite method with 108 references. He claims 0.5 to 0.8% accuracy for a proposed method at potassium levels above 5 mg. Shawarbi (*119*) describes a colorimetric dipicrylamine method applicable to a range of 10 to 400 micrograms of potassium. Either fading in color of reagent or color of an acetone solution of the precipitate may be measured.

Lithium was studied by Grüttner (*33*), who compared the phosphate, sulfate, aluminate, and zinc triple acetate precipitations. The acetate reagent is recommended. Not more than 2.3 mg. of lithium should be present in the aliquot taken for analysis. The separation of sodium and lithium by extraction of mixed chloride with amyl alcohol is excellent. Wilberg (*132*) presents a flame photometric procedure for lithium covering the range 0.04 to 0.20 milliequivalent. Potassium gives a positive interference. The necessary correction is easily determined with standard solutions.

SULFATE AND CHLORIDE

Munger, Nippler, and Ingols (*86*) present a determination of sulfate involving the titration of excess barium with ethylenediaminetetraacetic acid after the precipitation of barium sulfate. As the dye, Eriochrome Black, does not function as a barium indicator, it is necessary to add standard magnesium at the end of the titration (magnesium is also added to the titrant to provide sufficient concentration for obtaining a preliminary end point) and the titration is carried on to the second magnesium end point, which is sharper than the first. Correction is made for added magnesium and the total hardness of the sample.

Quevedo (*106*) describes the conductometric titration of sulfate in water. Calibration curves are prepared with solutions having nearly the same initial conductivity as the unknown. Concentrated waters are diluted to a working range of 200 to 800 micromhos. Honda (*45*) describes nephelometric determinations of sulfate with gelatin as suspending agent and the use of ion exchange to remove sulfate impurities in the gelatin. McConnell and Ingols (*74*) give detailed instructions for the determination of sulfate with benzidine hydrochloride.

Kolthoff and Kuroda present a potentiometric titration with silver nitrate (*51*) and an amperometric titration (*52*) suitable for the very low concentrations of chloride found in natural waters. The potentiometric procedure which is applicable down to 0.4 p.p.m. has the advantage in simplicity and suitability for routine use. The titration is made directly to the apparent equivalence potential. A supporting electrolyte of sodium nitrate and nitric acid is used. The amperometric method employs the rotating platinum electrode and gelatin for the supression of maxima, and does not require the removal of oxygen from solution.

Sakaguchi (*112*) studied the use of adsorption indicators for the argentometric titration of halides. He recommends tetrabromophenolphthalein ester for the chloride and iodide titrations and states that it can be used with 0.0025 N chloride solutions. Cyanosin is recommended for bromide. Clarke (*17*) in an addendum to a previous description of the chloride titration with mercuric nitrate describes the preparation of the reagent and the effect of pH on the titration.

FLUORIDE

An interesting determination of the fluorine content of monofluorinated organic compounds found in water is presented by Salsbury *et al.* (*113*). The method is applicable to studies of fluoride "take up" by organic pollutants in connection with fluoridation programs for control of dental caries. Pure fluorinated organics were used as reference compounds in the determinations which involved decomposition with a mixture of potassium metaperiodate, silver perchlorate, and perchloric acid, and distillation of the liberated fluorine as silicon tetrafluoride, followed by titration with thorium nitrate using Solochrome Brilliant Blue BS as indicator. With a 20-ml. sample, fluoride as low as 2 p.p.m. can be determined. There is no interference from ions commonly found in water. Aluminum shows no "holding" effect in the distillation. A colorimetric procedure is also given.

A modification of the Sanchis fluoride determination is proposed by Boonstra (*9*). Raising the ratio of alizarin to zirconium to 6 increases the sensitivity sixfold and reduces phosphate interference to a negligible quantity. The color is measured at 530 mμ on the spectrophotometer.

Taras (*125*) discusses the elimination of interference by dissolved chlorine, aluminum, and manganese dioxide in the Sanchis method. A publication by Busch, Carter, and McKenna (*13*) of the National Nuclear Energy Service describes a critical and comprehensive study of available fluoride determinations. Although most of the methods are applicable to high fluoride concentrations, some are sufficiently sensitive for the very low concentrations encountered in water.

NITRATE, AMMONIA, AND CYANIDE

A colorimetric determination of nitrate ion showing unusual sensitivity is presented by Gritsuya (*32*). Hydrostrychnine is used in a solution adjusted to pH 5. Interferences are controlled by the addition of tartaric acid, malonic acid, and citric acid. Minimum nitrate detectable is 0.02 p.p.m. Blom and Schwartz (*8*) describe the use of nickel ammonium sulfate solutions as the ammonia absorber in the Kjeldahl determination of ammonia and nitrates. Several amine-forming salts were investigated.

An improved Berthelot procedure for the determination of ammonia is described by Kulenok (*56*). The author recommends the use of thymol and hypobromite in place of phenol and hypochlorite.

Milne (*81*) discusses precautions necessary for the preservation of cyanide in samples of natural water. Protection from oxidation, high pH, and low temperature are necessary.

SELENIUM

A selenium procedure which uses complexing agents for the elimination of interference at moderate levels and requires distillation only at unusually high interference levels is described by Lambert, Arthur, and Moore (*62*). Final estimation is made spectrophotometrically after reaction with iodide, by measurement of absorption of the iodide-iodine complex at 352 mμ, measurement of the color developed with "cadmium iodide–linear starch reagent," or precipitation and collection of the starch blue in a confined spot test apparatus (*63*). Preparation of the starch reagent and uses as indicator for oxidants and iodide are given in other papers (*60, 61*).

A colorimetric selenium determination in which cation exchange resin is used for the separation from interferences is described by Yoshino (*133*). Selenite passes through quantitatively at pH 0.7 to 5.0. Separation from zinc is excellent, but iron cannot exceed ten times the selenium concentration. Selenium can be "gathered" by coprecipitation with zinc hydroxide and then separated from zinc in the cation exchange column.

Vanossi (*129*) presents a selenium determination in which the free element is concentrated by collection at the water-chloroform interface after distillation. As little as 0.1 microgram of selenium can be detected and the author suggests a lower limit of 0.01 microgram by using the catalytic effect of selenium on the reduction of gold by stannous chloride.

FREE CHLORINE AND CHLORAMINES

Marks, Williams, and Glasgow (*77*) point out the essential advantages of the amperometric determination of free chlorine and chloramines over the Palin method of titration with ferrous ammonium sulfate. Good results were obtained by Palin's method in the free chlorine titration, but titration of chloramines required low temperature and the end point faded rapidly. Reaction of free iodine with the *o*-tolidine indicator was the suspected cause of fading. In contrast, the amperometric titration (authors propose phenylarsenoxide in place of the customary arsenite) gives sharp end points and good differentiation among chlorine, monochloramine, and dichloramine, and can be done automatically. This automatic means of checking residual chlorine concentration is described by Hazey (*38*) in an account of the use of an automatic Wallace and Tiernan residual chlorine recorder at the Wyandotte plant.

A comparison of familiar methods of determining free chlorine concentration was made by Lur'e and Nikolaeva (*72*), who studied the iodometric, methyl orange, arsenite-tolidine, and *p*-aminodimethylaniline methods. All give accurate results, the authors state, and methyl orange gives the best differentiation between chlorine and chloramines. Houghton (*47*) studied the effect of pH on the chlorine-chloramine ratio and outlined analytical methods for following the chemistry of chlorine treatment.

DISSOLVED OXYGEN

In the continuing search for improved determinations of dissolved oxygen, a careful study of the acid-chromous method by Stone and Eichelberger appears to have considerable significance (*124*). Dissolved oxygen reacts to give trivalent chromium. Iodate is added in excess to react with the excess of chromous ion and the unreacted iodate is converted to iodine and titrated with thiosulfate in presence of starch. The elimination of nitrite interference is described. Checks against very carefully prepared standard oxygen solutions give excellent agreement with the values adopted by the American Public Health Association.

Verbestel, Berger, and Royer (*130*) report a critical study of dissolved oxygen determinations suitable for concentrations in the 0.01 p.p.m. range. The Winkler method was unsuitable at these extreme dilutions. An improved spectrophotometric *o*-tolidine procedure is recommended. Oxygen-free water was prepared by use of a cation exchange resin containing copper.

A polarographic determination is reported by Seaman and Allen (*116*), in which the diffusion current is measured before and after deaeration with nitrogen. Potassium chloride is used to raise the conductance, suppress the diffusion current maxima, and minimize the effect of variations in natural conductance of samples.

March (*76*) describes in detail, sufficient to permit reproduction from data given, a portable, polarographic dissolved oxygen meter using a rotating platinum electrode. The instrument was designed for natural brines and the author reports that to date attempts to use the instrument with natural waters by adding sodium chloride in sufficient amount to raise the ionic content to brine values have not given satisfactory results. Good linearity is reported in checks made by diluting brines with deaerated water.

Young, Pinckney, and Dick (*135*) made a study of the Winkler method, Schwartz-Gurney modification, and potentiometric methods and recommend the use of potentiometric determinations. Other studies are reported by Splittgerber *et al.* (*123*) and Meyer and Brack (*80*). A paper describing in considerable detail the commonly used methods was given by Leclerc, Beeckmans, and Beaujean (*65*).

OXYGEN CONSUMED AND BIOCHEMICAL OXYGEN DEMAND

A publication by Moore, Ludzack, and Ruchhoft (*82*) appears to be a significant contribution toward easing the chronic state of uncertainty in the determination of the "oxygen-consuming" power of natural water. The authors made a careful statistical study of the permanganate, iodate, chromate, and chromate plus silver sulfate methods. Both pure organics and trade wastes were used as standards for comparison. The authors' results, obtained with ten replicates on each run, show the superiority of the acid dichromate method using silver sulfate catalyst as recommended by Muers (*84*) from the standpoints of reproducibility and average percentage of theoretical oxidation.

Two sources report that the acid-chromate procedure gives reasonably close agreement with the 5-day B.O.D. values. Chakravarti and Som (*16*) compared the two methods on three types of waste and found slightly higher average results by acid chromate. The difference is attributed to presence of humus, cellulose, and other substances that are not oxidized biologically. They also studied the effect of temperature on the acid-chromate method and found a nearly linear increase in oxidation rate with temperature but wide variation in rate of increase between various kinds of wastes. Rhame (*109*) made similar comparisons between "oxygen consumed" by acid-dichromate and B.O.D. and found good agreement when an ammonia correction was made.

Medalia (*79*) studied the application of the autoxidation reaction of organic groups in the presence of hydrogen peroxide and ferrous ion as a possible oxygen consumed method. Oxidation was far short of theoretical in all tests with knowns and the method in the present state of development seems suited only for qualitative detection of presence of organic matter. Sensitivity for trace amounts of organic matter is good. The author studied the acid-chromate–silver sulfate method and permanganate method also as means of comparison; results show about 60% of theoretical oxidation on the average with the former method and the unusually low figure of less than 10% oxidation with the latter.

Pirogova (*97*), using an alkaline pretreatment, reports oxidation ranging from 65 to 90% of theoretical in the permanganate determination of oxygen consumed values for solutions of carbohydrates, proteins and fatty acids.

Two authors have reported on the toxic effect of traces of metals on the bacterial decomposition of waste. Heukelekian (*42*) studied the problem using both the dilution method and direct oxygen consumption. Dawson and Jenkins (*20*) used the Warburg manometric apparatus and reported highest toxicity with zinc, copper, chromium, cadmium, and nickel. Anions and organics were studied and in general toxic effects were not noted.

Other studies are reported by Skopintsev and Mikhailovskaya (*121*), Malchow-Møller (*75*), Van Meter, Gerke, and Buswell (*14*, *128*), and Porges and coworkers (*100*).

ORGANIC MATTER

A significant study of the nature of organic pollutants in natural water is presented by Braus, Middleton, and Walton (*11*), who have made the first extensive effort to apply the systematic methods of organic qualitative analysis to the characterization of organic compounds in water. Organic matter was collected by adsorption in tanks containing activated charcoal. The flow of water through the tanks was metered. A considerable range was found in the adsorption efficiency of commercial brands of charcoal. Organic matter was extracted from the charcoal with ether, weighed, and then subjected to qualitative analysis according to the scheme of Shriner and Fuson. The presence of phenols, rosin-type compounds, pyridines, pyrroles, and aliphatic hydrocarbons was established.

The application of infrared spectrophotometry to the determination oil and phenols in water is reported by Simard *et al.* (*120*). Use of infrared permits the determination of as little as 0.1 p.p.m. of oil and 10 p.p.b. of phenol. Phenols are determined by bromination, followed by extraction with carbon tetrachloride. Because of the high affinity of the lower molecular weight phenols for water, it is not possible to make a direct extraction with omission of the bromination step. The absorption of the extract is measured at 2.84 microns for the phenol determination and at the 3.4-micron region for oils. For calibration purposes standards should be prepared from synthetic mixtures that approximate the composition of the oil pollutant as closely as possible. When composition of the pollutant is undetermined, the authors recommend the use of an iso-octane, cetane, and benzene calibration mixture. Using this mixture, difficulties are encountered with lower aromatics because of the weak C—H aromatic absorption in the 3.4-micron region.

Musante (*87*) describes a significant modification of the conventional benzene extraction-evaporation procedure for the determination of oil in water. It is shown that enormous losses occur through prolonged heating past the point of complete removal of benzene solvent. Distillation is recommended for solvent removal, and a procedure is given which involves a preliminary macrodistillation for removal of the bulk of solvent, followed by microdistillation. It is not possible to attain complete removal of solvent; hence a blank is always run. Recovery with knowns ranged from 72 to 136% with an average of 102.6%.

RADIUM, RADIOACTIVITY, AND URANIUM

The separation of radium from barium and other elements is described by Tompkins (*127*). The sample is passed through a cation exchange resin and the radium and barium are eluted fractionally with solutions of various saturated polycarboxylic acid salts. The fractions are analyzed radiometrically.

An outline of methods used to estimate radiometric strontium, barium, cobalt, and iodine is presented by Duncan and coworkers (*22*). In general, the methods are conventional. Strontium and barium are brought down as chromates and converted to carbonates for counting. The cobalt is separated by extraction as the thiocyanate in amyl alcohol–ether, and is converted to ferrocyanide for counting. Iodide is precipitated with silver for counting after extraction with carbon tetrachloride.

Fields and Pyle (*27*) present a survey of the fundamentals of determining the micro quantities of radioactive isotopes found in natural waters. The techniques involved in the determination of a typical alpha and beta emitter are discussed in considerable detail, using uranium as the example of a typical alpha emitter and iodine as the typical beta emitter. Fluorometric determination of uranium concentration by "gathering" and pulse analysis are discussed. The discussion of the beta emitter covers use of a "carrier," conditions for accurate count, corrections for back-scattering, beta absorption, background beta emission, etc.

Gübeli-Litscher and Kolb (*34*) discuss determination of radium and thorium in spring waters. The sample is equilibrated with the gaseous phase by continuous circulation in closed system and the activity of the gaseous phase is measured in ionization chambers. The same type of determination is discussed in detail by Fineman and coworkers (*28*), who use a stream of argon for sweeping the radon into the alpha-ionization chambers.

Two papers offer ideas and information useful to anyone dealing with radioactivity in water, but have only an indirect analytical significance. Eliassen and coworkers (*24*) discuss the removal of dangerous isotopes by column techniques, and Lauderdale and Emmons (*64*) assess the value of conventional treatments in decontamination of public supplies.

A new chemical test for uranium is reported by Dasgupta and Gupta (*19*), who used oxalohydroxamic acid for the quantitative determination. An orange color is measured at 420 mμ. Limit of identification as a spot test procedure is 0.2 microgram and the dilution limit is 1 to 240,000. Nakanishi (*88*) describes the microdetermination of uranium by means of fluorescence in a sodium fluoride bead. Limits of detection are 0.1 microgram photographically and 0.001 microgram by visual comparison with standard beads. Maximum fluorescence is at 555.4 mμ.

MISCELLANEOUS

A boron test of unusual sensitivity is presented by Hegedus (*39*).

To 1 ml. of sample add 16 ml. of sulfuric acid and heat to fumes. Cool below 100° C., add 2 ml. of azo dye (0.12 ounce of chromotrop 2 B in 500 ml. of sulfuric acid), dilute with sulfuric acid to 15 ml.; keep for 30 minutes at 100° C., cool, and add 0.04 ml. of sodium cobaltinitrite solution. Shake well and keep for 8 hours in darkness. Read color in photometer. Sensitive to 0.25 microgram.

Jewsbury and Osborn (*49*) describe the photometric determination of boron with morin. Interferences and optimum conditions are discussed. The range covered is 20 to 200 micrograms.

Hegedus and Hegedus (*40*) describe a volumetric determination of arsenic based on the Marsh test. About 0.1 p.p.m. of arsenic can be detected. The theoretical factor for the ratio of potassium iodate to arsenic gave low results and an empirical factor was used.

Data are presented by Buneev (*12*) on the determination of dissolved gases in mineral waters. Laboratory analyses of gases are often not accurate.

Nümann (*89*) gives directions for colorimetric determination of silicates, organic and inorganic phosphorus, and nitrogen in sea water. Modifications of standard methods are recommended.

Field tests for the usual sanitary analyses are described by Schroeder (*115*) and a portable field kit and suitable chemicals are presented by Drachev (*21*).

Studies of the silicomolybdate method for high concentrations of silicon in natural waters are reported by Aoki (*1*).

Mundy, Burns, and Samuel (*85*) have conducted a review of conventional methods for water analysis.

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[End of Review Section]

TITRATIONS IN NONAQUEOUS SOLUTIONS

General and Round-Table Discussions Held by Division of Analytical Chemistry, 119th Meeting, American Chemical Society, Cleveland, Ohio, April 1951

Potentiometric Titration of Salts of Organic Bases in Acetic Acid

Salts of Amines, Basic Heterocyclic Nitrogen Compounds, and Quaternary Ammonium Compounds

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The advantage of using perchloric acid for the titration of organic bases in glacial acetic acid was first demonstrated by Conant and Hall (*2*, *7*). Conant and Werner (*3*) and Hall (*6*, *8*) determined the strength of organic bases in glacial acetic acid with perchloric acid. Hammett and Dietz (*9*) used formic acid as solvent, while La Mer and Downes (*15*) described conductometric and electrometric titrations in benzene. Perchloric acid was used for the visual titration of amino acids by Nadeau and Branchen (*17*) with crystal violet as indicator. Blumrich and Bandel (*1*) applied perchloric acid titrations in glacial acetic acid for the determination of primary, secondary, and tertiary amines, aliphatic bases, and alkaloids. Fritz (*4*, *5*) titrated many organic bases in nonaqueous solvents with perchloric acid in dioxane or acetic acid. Palit (*18*) determined alkali metal salts of weak monobasic organic acids in a mixture of solvents by perchloric acid titration.

Titration of Salts of Organic Bases (except hydrochloric, hydrobromic, and hydroiodic acid salts). Plati and Ingberman (*20*) reported that organic acid salts of organic bases could be titrated potentiometrically in glacial acetic acid with perchloric acid. Markunas and Riddick (*16*) investigated the titration of carboxylic acid salts in glacial acetic acid and titrated bases and salts of weak acids. The authors found that salts of organic bases with strong acids other than halide acids could also be titrated potentiometrically.

Titration of Halide Acid Salts of Organic Bases. Halide acid salts could not be titrated. [After this manuscript had been written, two papers by Higuchi and Concha (*10*, *11*) appeared, in which the visual titration of alkali chlorides and hydrochlorides with perchloric acid is described; the reaction is driven to completion by repeated boiling. Higuchi and Concha also studied the behavior of some inorganic anions in glacial acetic acid.] The authors' main objective was the development of a procedure to overcome this obstacle, as most of the physiologically active compounds are prepared as their water-soluble halide acid salts and a method for their direct titration was highly desirable. They were able to titrate halide acid salts of organic bases with perchloric acid by potentiometric or visual procedure after converting the salt to the acetate through the use of mercuric acetate.

No method for potentiometric titration of halide acid salts of organic bases has been reported, and only limited information on titration of salts of other strong acids with organic bases has been available. The proposed method permits the direct titration of salts of organic bases and halide acids (hydrochloric, hydrobromic, and hydroiodic) when mercuric acetate is added to the solution of the sample in glacial acetic acid prior to the titration with perchloric acid in dioxane. This titration can be carried out potentiometrically or visually, using crystal violet as indicator. Salts of organic bases with strong acids other than halide acids can be titrated without the addition of mercuric acetate. This rapid method has been applied to numerous alkaloids and several vitamins. Depending upon the sharpness of the potential break, a precision of ±0.2% can be obtained for many compounds. In the pharmaceutical industry a large number of compounds are prepared as water-soluble halide acid salts. The basic part of such salts usually constitutes the physiologically active component, for which no direct titration method existed. The proposed method will determine this basic part of the molecule, permitting the rapid assay of many pharmaceutical preparations with elimination of tedious extractions and colorimetric procedures. While the accuracy of the method is comparable to that of conventional methods, its sensitivity permits titrations with 0.01 *N* perchloric acid in dioxane in numerous cases.

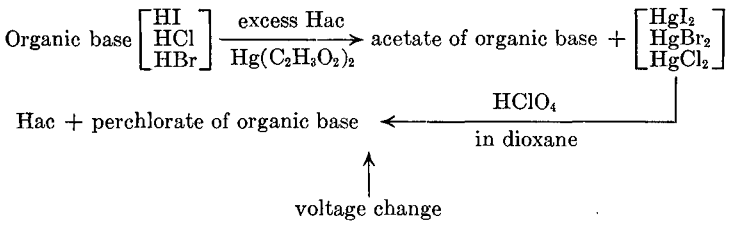
Kolthoff and Willman (*13*) had determined the dissociation constants of some inorganic acids, bases, and salts in glacial acetic acid and listed the inorganic acids in the following order of decreasing dissociation:

$$HClO_4 > HBr > H_2SO_4 > HCl > HNO_3$$

Kolthoff and Willman (*14*) also presented data concerning the basic strength of inorganic acetates and the strength of cations and anions in acetic acid. From these conductance measurements it was noted that mercuric acetate showed the lowest equivalence conductivity of any salt tested. This observation suggested the idea of adding mercuric acetate to the solutions of halide acid salts of organic bases in glacial acetic acid prior to their titration with perchloric acid. It was thought that the mercuric salts formed would exhibit a low conductivity and low dissociation in accordance with Kolthoff and Willman's postulations. The resulting experiments gave support to these theoretical considerations.

Mercuric salts were the only compounds tested that exhibited the combined qualities of low conductance and ability to bind halogen anions without affecting the potentiometric titration of the basic portion of the salt, using perchloric acid. Cations of the same group as mercury, such as silver and lead in the form of acetates, were tested because they also can bind the anions mentioned above. However, silver and lead acetate were found to consume perchloric acid. The halogens formed with silver and lead acetate were only slightly soluble in glacial acetic acid, while the mercury halides were soluble. When a compound of known purity was titrated with the substitution of a known quantity of lead acetate for mercuric acetate (in excess of the molar ratio), the amount of perchloric acid consumed was equivalent to the quantity calculated for the organic salt plus the excess of lead acetate added. This fact eliminated the practicability of using these cations, as it would be impossible to use them in excess of the molar ratio, whereas an excess of mercuric salts had no effect upon the potentiometric titration.

The reaction is believed to proceed in the following manner:



METHOD

Apparatus. Beckman pH meter, Model G, Fisher Senior Titrimeter, or similar potentiometric titrator.

Beckman glass electrode No. 1190–90.

Beckman Calomel Electrode, No. 1170. Calomel electrodes were observed to be easily contaminated by mercuric acetate in glacial acetic acid, causing fluctuation of the galvanometer needle. If this condition occurs, the saturated potassium chloride solution inside the electrode should be removed, and the cell should be flushed with distilled water, rinsed with saturated potassium chloride solution, and refilled with saturated potassium chloride solution.

Reagents. Perchloric acid, 0.1 *N*, in dioxane, is prepared by dissolving approximately 8.4 ml. of 70 to 72% perchloric acid in 1 liter of dioxane. This solution is standardized by titration against National Bureau of Standards potassium acid phthalate as described for the sample (*16, 21*).

Glacial acetic acid, C.P.

Mercuric acetate reagent is made by dissolving 6 grams of C.P. mercuric acetate in 100 ml. of hot glacial acetic acid and cooling to room temperature.

PROCEDURE

A sample of appropriate size, to require a titration of approximately 30 ml. of 0.1 *N* perchloric acid in dioxane is weighed into a 250-ml. beaker. To calculate the approximate weight of sample, the following equation may be applied:

$$\text{Sample weight (grams)} = 30 \times 0.1 \times \text{milliequivalent weight of compound}$$

This calculation can be simplified by drawing a nomograph from the above formula, plotting milliequivalent weight against weight of sample.

As it is believed that the sharpness of the end point is dependent upon the electrical conductivity, dioxane being nonconductant, the ratio of acetic acid to dioxane in the standardization and the test should be kept fairly constant. For this purpose the authors generally used a uniform quantity of 80 ml. of glacial acetic acid (including the mercuric acetate solution) for solubilizing the sample.

Potentiometric Titration. If the sample does not dissolve readily, the mixture may be heated to boiling. Under these conditions almost all finely powdered samples dissolved completely. If the sample is a salt of an organic base, other than a halide acid salt, the solution may be titrated after cooling to below 75° C.

However, if the sample is a hydrochloride, hydrobromide, or hydroiodide of an organic base, 10 ml. of mercuric acetate reagent should be added to the acetic acid solution after cooling to room temperature.

The solution is titrated with 0.1 *N* perchloric acid–dioxane solution, using the millivolt scale of a potentiometric instrument. The millivolts, *E*, are recorded every 0.1 ml. in the vicinity of the calculated end point (Figure 1). The exact end point is determined by plotting a graph of $\Delta E/\Delta V$ *vs.* V (ml.). From the extrapolated curve the milliliters of 0.1 *N* perchloric acid consumed are obtained (Figure 2).

Visual Titration. Various investigators (*3, 16, 17, 21*) advocated the use of crystal violet as visual indicator for acid-base titrations in glacial acetic acid. This indicator was found to be very suitable for routine titrations of compounds that give a sharp potentiometric break.

Procedure. A sample of appropriate size is weighed and dissolved in glacial acetic acid as described under potentiometric titration. If heating is required for the complete solution of the sample, the solution must then be cooled to room temperature.

In the case of salts of halide acids, 10 ml. of a mercuric acetate reagent are added at this point, followed by 0.5 ml. of the crystal violet indicator (0.1% in glacial acetic acid). The solution is then titrated with 0.1 *N* perchloric acid–dioxane, preferably under mechanical stirring. The correct shade of the end point must be previously determined by visual standardization against the primary standard and the color matched in the titration of the sample.

DISCUSSION

Effect of Temperature. No noticeable effect on the potentiometric end point was observed when the titration was run either at room temperature or in hot solutions. Most of the determinations were therefore carried out after cooling to below 75° C., but without control of the temperature at a constant level. However, in the case of sensitive substances, such as thiamine hydrochloride, it is advantageous to dissolve the sample in warm glacial acetic acid, cool it to room temperature, and then add 10 ml. of cold mercuric acetate reagent, so as to avoid decomposition.

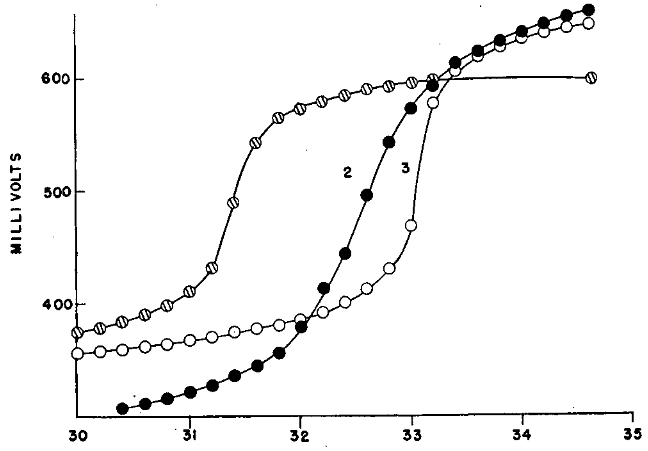


Figure 1. Titration Curves

1. **Papaverine hydrochloride**
2. **Morphine hydrochloride**
3. **Prostigmine bromide (neostigmine bromide)**

Effect of Excess Mercuric Acetate. When a 0.1 *N* perchloric acid solution was used as the titrant, quantities up to 3 grams of mercuric acetate could be used without deleterious effects (Table I). However, when small samples using 0.01 *N* perchloric acid are titrated, the quantity of mercuric acetate used should not exceed 2 moles per mole of the compound being titrated.

Table I. Effect of Mercuric Acetate upon Potentiometric Standardization of Perchloric Acid

Sample Weight	Mercuric Acetate Added	$HClO_4$ Consumed	Calculated Normality	Deviation from Mean
Gram	*Gram*	*Ml.*	*N*	*N*
		Anhydrous Sodium Carbonate		
0.2024	.....	38.70	0.09868	+0.00003
0.2028	.....	38.80	0.09862	−0.00002
0.2094	.....	40.05	0.09865	±0.00000
		Av.	0.09865	
0.2041	0.3	39.00	0.09874	+0.00010
0.2024	0.6	38.75	0.09855	−0.00009
0.1998	0.6	38.25	0.09856	−0.00008
0.2044	0.6	39.10	0.09863	−0.00001
0.2020	3.0	38.60	0.09874	+0.00010
		Av.	0.09864	
		Anhydrous Potassium Chloride		
0.2255	0.3	30.65	0.09866	−0.00001
0.2247	0.6	30.55	0.09864	−0.00003
0.2267	1.2	30.80	0.09871	+0.00004
		Av.	0.09867	

Effect of 0.01 *N* Perchloric Acid as Titrant. As for most compounds the visual end point is not sufficiently sharp when 0.01 *N* perchloric acid is used, only potentiometric titrations should be conducted at that concentration.

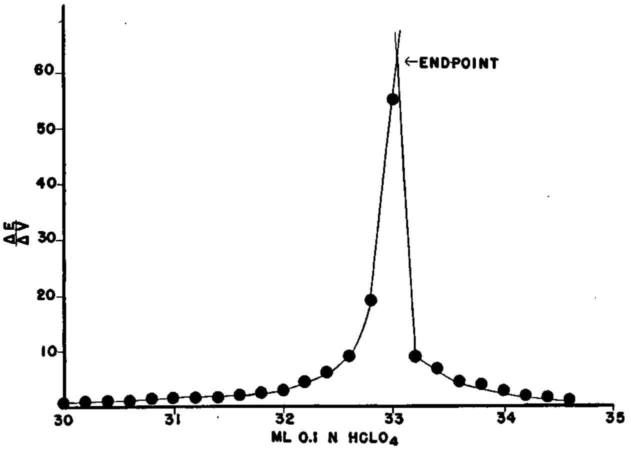


Figure 2. Titration of Prostigmine Bromide

Effect of Solvents for Perchloric Acid. In this work, perchloric acid in dioxane was used as the titrant. With 0.1 *N* solutions, a titrant prepared with glacial acetic acid instead of dioxane will result in a slight decrease of sensitivity, which becomes very apparent when 0.01 *N* perchloric acid is used (Figure 3). A comparison of the ratio of dioxane to glacial acetic acid in titrations with 0.01 *N* perchloric acid is presented in Figure 4.

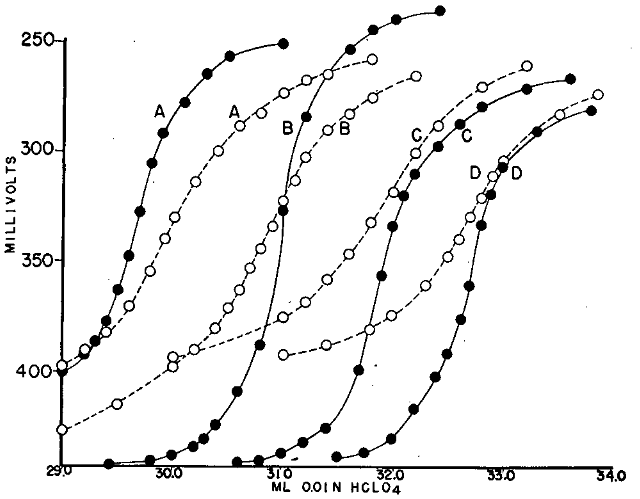


Figure 3. Potentiometric Titrations with 0.01 *N* Perchloric Acid

● **In dioxane**
○ **In glacial acetic acid**
A. **Asterol.2HCl**
B. **Pyridoxine.HCl**
C. **Thiamine.HCl**
D. **Neostigmine bromide**

It is evident that the sharpness of the potentiometric break is enhanced with increased concentration of dioxane. This might well be due to the decrease in equivalence-conductance of the glacial acetic acid mixture, caused by the dilution with dioxane. When the total concentration of glacial acetic acid is decreased to less than about 15%, it becomes difficult to conduct a potentiometric titration, as the solution approaches the status of a nonelectrolyte.

This effect of greater sensitivity and the ease of handling dioxane prompted its use as a diluent for perchloric acid. As the

Table II. Comparison of Results Obtained with Perchloric Acid Dissolved in Dioxane and Acetic Acid

Solvent	Normality of Standardization Pot.	Normality of Standardization Vis.	Asterol Dihydrochloride, % Pot.	Asterol Dihydrochloride, % Vis.
Dioxane				
Sample 1	0.1001	0.0997	99.76	99.82
Sample 2	0.1001	0.0997	99.74	99.80
Av.			99.8	99.8
Acetic acid				
Sample 3	0.0993	0.0989	99.86	99.91
Sample 4	0.0993	0.0989	99.87	99.93
Av.			99.9	99.9

coefficient of expansion of dioxane is greater than that of glacial acetic acid, which in turn has a coefficient approximately five times that of water, temperature fluctuations tend to have a distinct effect upon the normality factor of the titrant. For this reason the perchloric acid titrant should be standardized daily and if considerable variations in temperature occur during the day, a correction for the change in volume should be applied.

Results obtained by both potentiometric and visual titration of 2-dimethylamino-6-(β-diethylaminoethoxy)-benzothiazole (Asterol) dihydrochloride, using 0.1 *N* perchloric acid in dioxane, as well as in glacial acetic acid, are reported in Table II.

From these results it is evident that the visual normality factors are slightly lower than those arrived at by potentiometric titration. However, when these potentiometric or visually determined normality factors are applied to potentiometric or visual titrations of the sample, the results obtained remain within the limit of the experimental error.

Effect of Solvents in Pharmaceutical Preparations. Solvents commonly used in pharmaceutical preparations, such as ethyl alcohol, isopropyl alcohol, glycerol, propylene glycol, and Carbowax showed no interference with the titration.

Effect of Water. The presence of water should be avoided, because it impairs the sharpness of the end point. As is evident from Figure 5, the presence of 1% water in a titration of 600 mg. of Asterol dihydrochloride in a total of 100 ml. of solvent caused a slight flattening of the titration curve. Larger quantities of water completely interfered with a sharp end point. In order to obtain sharp potentiometric breaks, the amount of water present should be limited to less than 1% per titration when 0.1 *N* perchloric acid solutions are used. However, it was possible to eliminate as much as 10 ml. of water per sample titrated by adding an excess of acetic anhydride directly to the sample, heating the mixture to boiling for approximately 5 minutes, and then bringing the volume to 80 ml. with glacial acetic acid. An excess of acetic anhydride had no effect upon the potentiometric titration. This procedure cannot be applied to salts of primary or secondary amines, which would be acetylated and consequently could not be titrated with perchloric acid.

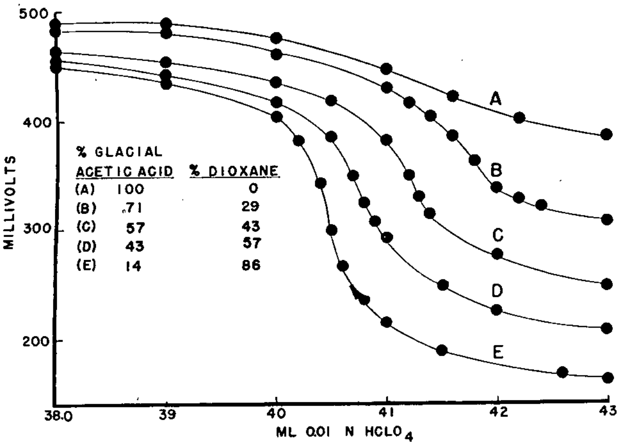


Figure 4. Effect of Ratio of Glacial Acetic Acid to Dioxane upon Potentiometric Titrations

0.01 *N* perchloric acid

Effect of Mercuric Salts. The presence of mercuric bromide, chloride, and iodide in these titrations caused no interference, as the electrical conductivity of mercuric salts is very low.

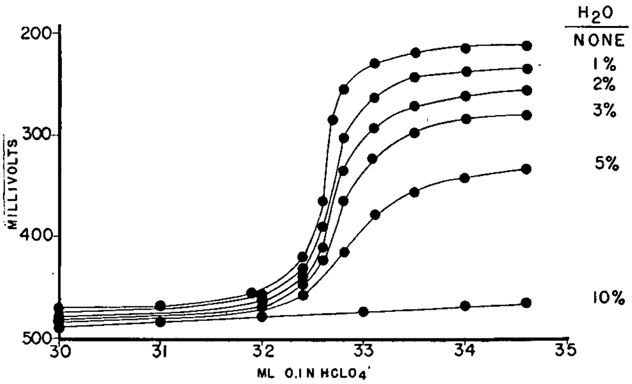


Figure 5. Effect of Water upon Potentiometric Titration Curve

Sample. 600 mg. of Asterol dihydrochloride in 80 ml. of glacial acetic acid

Effect of Cations. Almost all cations, other than mercuric compounds, will interfere with the titration, owing to their reaction with perchloric acid.

Effect of Organic and Inorganic Acids. It was found that the reaction between the organic base and perchloric acid takes place stoichiometrically and is independent of the amount of free acid (either organic or inorganic) present.

RESULTS

The method described was applied to a great number of salts of organic bases. Results obtained on salts of amines are listed in Table III. Histamine and histidine salts were found to be difficult to solubilize. Gentle heating and prolonged stirring in glacial acetic acid were required to obtain a complete solution. The procedure is also applicable to many antihistaminic compounds.

Table III. Amine Salts

	Perchloric Acid Titration, %[a]	Extraction of Base and Titration of Extract, %[a]
Desoxyephedrine (*N*,α-dimethylphenethylamine) hydrochloride		
A	100.0	99.5
B	100.1	99.8
C	99.3	99.4
2-Dimethylamino-6-(β-diethylaminoethoxy)benzothiazole(Asterol) dihydrochloride		
A	100.0	99.7
B	99.9	99.6
C	100.0	99.8
Histidine monohydrochloride		
A	99.5	..
B	99.8	..
C	99.5	..

Additional amine salts successfully titrated by perchloric acid method:
Guanidine hydrochloride
1-*p*-Aminobenzoyl-2,2-dimethyl-3-diethylaminopropanol hydrochloride (Larocaine hydrochloride)
β-Diethylaminoethyl fluorene-9-carboxylate hydrochloride (Pavatrine)
Phenylbiguanidine hydrochloride
Quinacrine hydrochloride (Atabrine)
Histamine dihydrochloride
Hydroxylamine hydrochloride
Amphetamine sulfate
Ephedrine sulfate
1-(3,4-Dimethylphenyl)-2-aminopropane sulfate (Ro 2-1038-3)
Atropine nitrate
Histamine phosphate

[a] Anhydrous basis.

Values found for salts of basic heterocyclic nitrogen compounds are presented in Table IV. (As papaverine is too weak a base to be titrated in the conventional manner, no other comparable assay values for papaverine hydrochloride could be given.) It was observed that sulfates (Figure 6) titrated by this method consumed only 1 mole of perchloric acid, contrary to the 2 equivalents expected. Acid sulfates might be formed in these instances. A sample of quinine sulfate tested required 3 equivalents, as further proof of this fact.

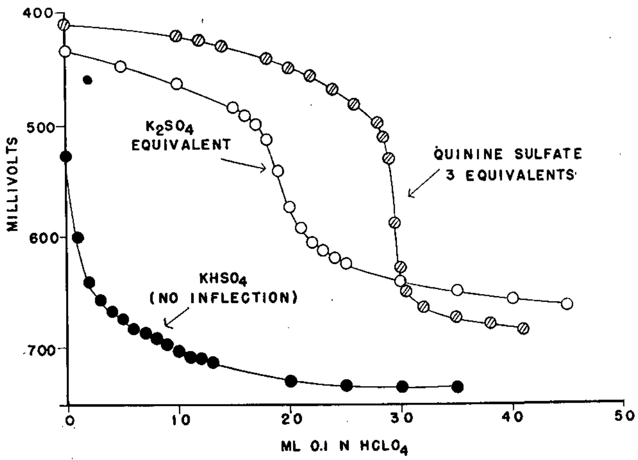


Figure 6. Sulfate Titrations with 0.1 *N* Perchloric Acid

$K_2SO_4 + HAc \rightarrow KHSO_4 + KAc$

Table IV. Heterocyclic Nitrogen Salts

	Perchloric Acid Titration, %[a]	
Papaverine hydrochloride		
A	100.0	
B	99.9	
C	99.9	
3-Pyridyl carbinol tartrate (Roniacol tartrate)		Colorimetric Method (*23*), %
A	99.9	99
B	99.8	100
C	99.9	100
Codeine phosphate (as anhydrous codeine base)		U.S.P. Method, %
A	73.3	72.9
B	72.9	72.6
C	73.6	72.8

Additional heterocyclic nitrogen salts successfully titrated by perchloric acid method:

Arecoline hydrobromide
dl-3-hydroxy-*N*-methyl morphinan hydrobromide (Dromoran hydrobromide)
Betaine hydrochloride
Codeine hydrochloride
Morphine hydrochloride
dl-α-1,3-dimethyl-4-phenyl-4-propionoxypiperidine hydrochloride (Nisentil hydrochloride)
Brucine sulfate
Caffeine sulfate
Morphine sulfate
Tropic acid-2,2-dimethyl-3-diethylaminopropanol phosphate (Syntropan phosphate)
2-Methyl-9-phenyl-2,3,4,9-tetrahydro-1-pyridindene tartrate (Thephorin tartrate)

[a] Anhydrous basis.

The method proved to be useful for the rapid titration of several vitamins containing basic heterocyclic nitrogen groups (Table V), for some of which only tedious fluorometric or colorimetric assay methods existed. Nicotinic acid and nicotinamide were included in this table because they also could be titrated in the manner described, although, not being salts, they do not come particularly within the scope of this paper. Typical e.m.f. curves for this group of vitamins are plotted in Figure 7.

Table V. Vitamins

	Perchloric Acid Titration, %[a]	U.S.P. Thiochrome Assay, %[a]
Thiamine hydrochloride (vitamin B_1)		
A	100.1	100.0
B	99.1	100.3
C	99.4	99.9
D	99.4	99.1
E	100.2	99.0
F	100.2	99.0
Pyridoxine hydrochloride (vitamin B_6)		Colorimetric Method (*12*), %
A	100.0	101.0
B	100.2	99.0
C	100.0	100.0
Niacinamide (nicotinic acid amide)		U.S.P. Method, %
A	99.7	99.8
B	100.0	100.2
C	99.9	100.0

Additional vitamin successfully titrated by perchloric acid method: Niacin (nicotinic acid)

[a] Anhydrous basis.

Table VI. Quaternary Ammonium Salts

	Perchloric Acid Titration, %[a]	U.S.P. Method, %[a]
Neostigmine bromide (Prostigmine bromide)		
A	99.5	98.5
B	99.6	98.8
C	99.9	99.7
Choline chloride		Precipitation as Reineckate (*19*), %
A	100.0	100.7
B	100.0	99.7
C	99.9	99.9
(3-Hydroxyphenyl)-ethyldimethyl ammonium chloride (Tensilon)		
A	99.9	..
B	100.1	..
C	99.9	..

Additional quaternary ammonium salts successfully titrated by perchloric acid method:

Cetylpyridium chloride
Triphenyl tetrazolium chloride
Tetraethyl ammonium bromide
(3-Hydroxyphenyl)-ethyldimethyl ammonium bromide (Ro 2-3198-1)
Dimethylcarbamate of (2-hydroxy-3-cyclohexylbenzyl)-methylpiperidinium bromide (Ro 2-0911)
Choline dihydrogen citrate
Choline dihydrogen tartrate

[a] Anhydrous basis.

Titration values obtained on quaternary ammonium salts are compiled in Table VI. Perchlorate titration is the only method perfected at present for the determination of (3-hydroxyphenyl)-ethyldimethylammonium chloride (Table VI), a stable and chemically rather unreactive quaternary ammonium salt.

ACCURACY AND PRECISION OF METHOD

The basic part of an organic salt is most frequently found to be its physiologically active portion. As the perchloric acid titration will determine just this part, the accuracy of the results may be considered equivalent to that obtained by more cumbersome conventional methods, such as the extraction of the base from alkaline solution and titration of the solvent extract (Tables III, IV, V, and VI).

The precision obtainable with this method on compounds giving a sharp potential break is exemplified in Table VII. A dried sample of pyridoxine hydrochloride was titrated on five different days with perchloric acid. The results indicate a reproducibility of ±0.2% for this compound. In a similar experiment, conducted with anhydrous thiamine hydrochloride, a precision of ±0.1% was obtained, using the Fisher Senior Titrimeter.

ADVANTAGES OF METHOD

The advantages of the method described over other procedures, used heretofore for the assay of many organic salts, are manifold.

The method is rapid and eliminates tedious extractions and other complicated procedures. It provides stoichiometric results without having to resort to standards, such as those used for colorimetric determinations. In some cases, such as for salts of weak bases or for unreactive quaternary ammonium salts, it offers the only direct assay method known.

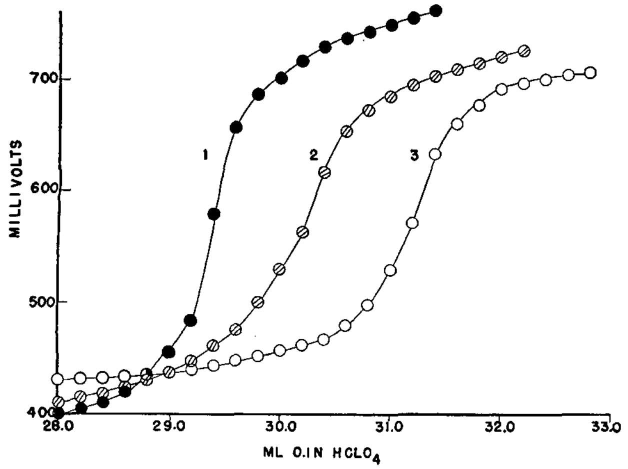


Figure 7. Titration Curves of Vitamins

1. Pyridoxine hydrochloride (vitamin B_6)
2. Thiamine hydrochloride (vitamin B_1)
3. Niacinamide

Application to Assay of Pharmaceutical Preparations. The advantage of using potentiometric titration for pharmaceutical control had been pointed out by Waters, Berg, and Lachmann (*22*). The proposed method can be easily adapted for the assay of pharmaceutical preparations, such as tablets, ampoules, ointments, and some solutions. As cations, such as sodium, magnesium, and calcium, will cause interference, their presence should be excluded, when this method is applied to pharmaceutical preparations.

Table VII. Reproducibility of Results

	Perchloric Acid Titration, %[a]	Deviation from Mean, %[a]
Pyridoxine hydrochloride		
1	100.1	+0.2
2	100.0	+0.1
3	99.9	0.0
4	100.0	+0.1
5	99.8	−0.1
Mean	99.9	
Thiamine hydrochloride		
1	99.7	0.0
2	99.6	−0.1
3	99.7	0.0
4	99.7	0.0
5	99.6	−0.1
Mean	99.7	

[a] Anhydrous basis

In the case of certain tablets containing a halide acid salt of an organic base and cations derived from a lubricant, such as magnesium or calcium stearate, interference due to these cations may be corrected for as follows:

After the sample is dissolved in warm glacial acetic acid and cooled to room temperature, the solution is titrated with perchloric acid in dioxane (blank titration, due to the cations in the tablet mass). Mercuric acetate reagent is then added and the titration is continued to the final end point. The value of the blank titration is subtracted from the total volume required.

Results obtained on tablets, ampoules, ointments, and alcoholic solutions are reported in Table VIII.

Table VIII. Pharmaceutical Preparations

Sample	Perchloric Acid Method: Pot. *Mg.*	Vis. *Mg.*	Av. *Mg.*	U.S.P. Method *Mg.*	Deviation *Mg.*
Neostigmine Bromide Tablets, 15 Mg.					
1	15.7	15.7	15.7	15.8	−0.1
2	15.9	15.8	15.9	15.7	+0.2
3	15.6	15.6	15.6	15.4	+0.2
4	15.7	15.4	15.6	15.2	+0.4
5	16.4	16.4	16.4	16.4	0.0
Syntropan Phosphate Ampoules, 10 Mg. per Ml.				Base Extraction and Titration *Mg.*	
1	10.6	..	..	10.7	−0.1
2	10.5	..	..	10.5	0.0
3	10.6	..	..	10.6	0.0
4	10.5	..	..	10.9	−0.4
5	10.6	..	..	10.4	−0.2
Asterol Dihydrochloride Ointment, 10%					
1	10.2	10.2	10.2	10.3	−0.1
2	10.3	10.2	10.3	10.2	+0.1
3	10.4	10.3	10.4	10.4	0.0
4	10.2	10.3	10.3	10.3	0.0
5	10.2	10.3	10.3	10.2	+0.1
Asterol Dihydrochloride Alcoholic Solution, 10%					
1	10.4	..	..	10.6	−0.2
2	10.4	..	..	10.5	−0.1
3	10.5	..	..	10.4	+0.1
4	10.4	..	..	10.6	−0.2
5	10.5	..	..	10.6	−0.1

Application to "Onium" Salts. The method was successfully applied to salts of onium-type compounds, such as diazonium and sulfonium salts. It is believed that the following onium salts would react in a similar manner:

Onium Salts	Empirical Formula
1. Quaternary arsonium salts	$[(C_nH_{2n+1})_4As]^+X^-$
2. Diazonium salts	$[\text{Aryl } N\equiv N]^+X^-$
3. Polyphenylchromium salts	$[(C_6H_5)_nCr]^+X^-$
4. Trialkyllead salts	$[(C_nH_{2n+1})_3Pb]^+X^-$
5. Phosphine and phosphonium salts	
Primary phosphine salts	$[C_nH_{2n+1}PH_3]^+X^-$
Secondary phosphine salts	$[(C_nH_{2n+1})_2PH_2]^+X^-$
Tertiary phosphine salts	$[(C_nH_{2n+1})_3PH]^+X^-$
Quaternary phosphonium salts	$[(C_nH_{2n+1})_4P]^+X^-$
6. Quaternary stibonium salts	$[(C_nH_{2n+1})_4Sb]^+X^-$
7. Sulfonium salts	$[(C_nH_{2n+1})_3S]^+X^-$
Sulfonium sulfides	$[R_3S]_2{}^+S^{--}$
Sulfoxides	$[R_2SOH]^+NO_3{}^-$
8. Tin salts	
Dialkyltin salts	$[(C_nH_{2n+1})_2Sn]^{++}2X^-$
Trialkyltin salts	$[(C_nH_{2n+1})_3Sn]^+X^-$

Application for Molecular Weight Determination. The molecular weight equivalents of amines and basic heterocyclic nitrogen compounds have been successfully determined by titrating their purified oxalates or tartrates by the method described. The molecular weight of an unknown base may be calculated by applying the following formula after titrating its oxalate with perchloric acid:

$$\frac{\text{Wt. of sample (grams)} \times 1000}{\text{ml. of } HClO_4 \times \text{normality}} - 90 \times \text{No. of equivalents} = \text{mol. wt. of unknown base}$$

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Titration of Certain Salts as Acids in Nonaqueous Solvents

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No existing method is entirely satisfactory for titration of acid bound to moderately strong bases. Salts of ammonia, aliphatic amines, and most other organic bases may be conveniently titrated as acids in ethylenediamine or dimethylformamide solution. Sodium methoxide in benzene-methanol serves as the titrant and either thymol blue or *p*-nitrobenzeneazoresorcinol (azo violet) is used as the visual indicator, depending on the solvent chosen. Titration of aqueous samples may be effected by first adding 15 to 20 ml. of ethylenediamine to a 1-ml. sample. The method should be particularly useful for the titration of ammonium and aliphatic amine salts.

THE mineral acid salts of most aromatic amines and other weak bases can be titrated in aqueous solution with sodium hydroxide. Difficulty is experienced, however, in titrating the salts of stronger bases, such as ammonia and aliphatic amines. Titration in the presence of neutral formaldehyde (*6*) or alcohol (*2, 7, 12*) often permits the determination of such salts, but these modifications are not universally successful.

Acid-base titrations in nonaqueous media are rapid, accurate, convenient, and very broad in scope. Several papers have dealt with the titration of weak bases in nonaqueous solvents (*1, 3, 5, 10, 11*); others with the titration of weak acids in ethylenediamine (*9*), butylamine, and benzene-methanol (*4*). Markunas and Riddick (*8*) titrated certain carboxylic acid salts as bases in glacial acetic acid solution. It is now proposed to determine certain salts by titration as acids in nonaqueous solvents.

METHOD

The salt is dissolved in an appropriate solvent and titrated with a 0.1 *N* solution of sodium methoxide in benzene-methanol. Either thymol blue or *p*-nitrobenzeneazoresorcinol (azo violet) is used as the indicator, depending on the solvent chosen. Almost without exception, the end points obtained are sharp and vivid.

REAGENTS AND SOLUTIONS

Benzoic acid, primary standard grade.

Dimethylformamide (DMF), technical grade (Du Pont).

Ethylenediamine, 95 to 100% as purchased commercially.

Salts were mostly commercial samples (99 to 100% purity), analyzed as received. The amine perchlorates were prepared by dissolving the amine base in ether and adding a solution of 72% perchloric acid in ether to precipitate the salt. The precipitate was then washed three times with ether and air dried.

Benzene-methanol. Four volumes of benzene were mixed with 1 volume of commercial absolute methanol.

p-Nitrobenzeneazoresorcinol was made by thoroughly mixing 0.2 gram with 100 ml. of benzene, warming, and filtering.

Sodium methoxide in benzene-methanol. A 0.1 *N* solution was prepared as described by Fritz and Lisicki (*4*). This solution is clear and essentially colorless, but sometimes separates into two layers on long standing. This may be corrected by the addition of a small amount of methanol.

Thymol blue, 0.3 gram of thymol blue dissolved in 100 ml. of methanol.

PROCEDURE

Most of the solvents employed contain acid impurities and should therefore be neutralized shortly before use. This is accomplished by adding enough indicator to impart a definite color to the solvent, then titrating with 0.1 *N* sodium methoxide to a clear blue end point. The sample to be titrated is weighed accurately into a 50-ml. beaker or flask, 15 to 20 ml. of neutralized solvent are added, and the solution is titrated with 0.1 *N* sodium methoxide to a clear blue color. During the titration the beaker should be covered to exclude carbon dioxide; mixing is best accomplished with a magnetic stirrer. The titrant is added from a 10-ml. buret which can be read accurately to 0.01 ml.; the sample weight is chosen so that 4 to 9 ml. of titrant will be required.

The sodium methoxide is standardized against pure benzoic acid using the above procedure. The titer of the sodium methoxide should be checked every 2 to 4 days.

SCOPE

Salts of the type B.HA can be titrated if the strength of the basic constituent, B, is not too great and if the acid, HA, is not too weak. Mineral acid salts of ammonia and aliphatic amines as well as aromatic amines gave very sharp end points in every case tried. Guanidine hydrochloride behaves as an acid, but the end point is very poor because of the strong base (guanidine) liberated during the titration. Trimethylphenylammonium iodide failed to react acidic to azo violet in any of the solvents tried. The strength of the acidic constituent of the salt may be fairly weak and still permit accurate titration—for example, ammonium benzoate gives as sharp an end point as ammonium chloride or ammonium sulfate.

Aqueous solutions can usually be titrated if the salt concentration is such that a sample of small volume can be used. Ethylenediamine is added in a volume ratio to water of at least 15 to 1 and the resulting solution is then titrated directly. A few salts such as carbonates, oxalates, and phosphates precipitate when the ethylenediamine is added and cannot be titrated by this procedure.

Data for the titration of representative salts are given in Table I.

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Table I. Titration of Salts with Sodium Methoxide

Salt	Solvent	Taken *Mg.*	Base *Ml.*	Base *N*	Indicator	Found %
Ammonium sulfate	H_2O-EN	59.6	8.34	0.1082	Azo violet	99.9
Ammonium sulfate	H_2O-EN	61.0	8.53	0.1082	Azo violet	99.9
Ammonium sulfate	H_2O-Morp.	45.7	8.01	0.0862	Thymol blue	99.8
Ammonium benzoate	H_2O-EN	64.3	4.30	0.1078	Azo violet	100.3
Ammonium benzoate	H_2O-EN	82.1	5.50	0.1078	Azo violet	100.5
Butylamine hydrochloride	H_2O-EN	70.8	5.96	0.1078	Azo violet	99.5
Butylamine hydrochloride	H_2O-EN	60.6	3.73	0.1471	Azo violet	99.2
Butylamine hydrochloride	H_2O-EN	85.4	5.26	0.1471	Azo violet	99.3
Dibutylamine hydrochloride	H_2O-EN	93.1	3.80	0.1471	Azo violet	99.5
Dibutylamine hydrochloride	EN	102.9	4.20	0.1471	Azo violet	99.4
Methylamine hydrochloride	EN	44.7	4.49	0.1471	Azo violet	99.8
Methylamine hydrochloride	H_2O-Morp.	36.7	6.33	0.0864	Thymol blue	100.6
Methylamine hydrochloride	H_2O-EN	37.0	6.35	0.0864	Azo violet	100.1
m-Phenylenediamine.2HCl	H_2O-EN	73.6	7.47	0.1082	Azo violet	99.3
Quinine sulfate.$2H_2O$	H_2O-EN	147.5	3.49	0.1082	Azo violet	100.1
p-Aminophenol.HCl	DMF	59.1	3.72	0.1088	Azo violet	99.7
p-Aminophenol.HCl	DMF	66.6	4.21	0.1088	Azo violet	100.1
Ammonium iodide	DMF	77.2	5.09	0.1016	Thymol blue	97.1
Ammonium iodide	DMF	67.9	4.46	0.1016	Thymol blue	96.6
Ammonium iodide	DMF	72.6	4.79	0.1016	Thymol blue	97.2
Aniline perchlorate	DMF	12.0	0.56	0.1095	Thymol blue	98.9
p-Bromophenylhydrazine.HCl	DMF	87.0	2.17	0.1790	Thymol blue	100.0
Caffeine citrate	DMF	107.1	7.63	0.1088	Azo violet	99.8
Caffeine citrate	DMF	78.9	5.63	0.1088	Azo violet	100.2
6-Nitroquinoline.$HClO_4$	DMF	6.0	0.20	0.1095	Thymol blue	100.2
Pyridine perchlorate	DMF	40.1	2.05	0.1095	Thymol blue	100.5
Pyridine picrate	DMF	77.6	2.28	0.1095	Thymol blue	99.3
Phenanthrene picrate	DMF	57.3	1.63	0.0860	Thymol blue	99.7

Abbreviations. EN = ethylenediamine; DMF = dimethylformamide; Morp. = morpholine.

CHOICE OF SOLVENTS

The general requirements of the solvent are that it be readily available, dissolve readily a large variety of salts, and possess almost no acidic properties. Alcohols are unsatisfactory because of their acidic properties. Many inert and basic solvents have very little acid strength, but most of these are poor solvents for salts.

Ethylenediamine (95 to 100%) is an excellent solvent for most salts and excellent end points can be obtained using azo violet indicator. It is particularly valuable when the sample is an aqueous solution. Solid salts such as ammonium sulfate, which do not dissolve readily in ethylenediamine or other organic solvents, may be dissolved in a small amount of water, ethylenediamine added, and the titration carried out without the formation of a precipitate. One disadvantage in the use of this solvent is that it absorbs carbon dioxide from the air with great avidity and thus must be handled with care.

Dimethylformamide is almost as good a solvent for salts as ethylenediamine. This solvent has recently been made commercially available at a reasonable price and the technical grade material is satisfactory. The following generalities regarding the solubility of salts in dimethylformamide can be made:

> Aromatic and higher aliphatic amine salts of organic and inorganic monobasic acids are soluble.
>
> Many ammonium and lower aliphatic amine salts of monobasic acids are also soluble.
>
> Ammonium nitrate, ammonium bromide, and ammonium thiocyanate are soluble; ammonium chloride, ammonium acetate, and butylamine hydrochloride are insoluble.
>
> Salts of polybasic acids are generally insoluble.

Pyridine, morpholine, benzene-methanol, and butylamine have been found useful for the titration of some salts.

CHOICE OF INDICATORS

Azo violet gives excellent end points (red to blue) in basic solvents and is the only indicator thus far tested which gives satisfactory results in ethylenediamine. This indicator gives sharp end points in dimethylformamide but not in inert solvents such as benzene and ether. Thymol blue is generally the most satisfactory indicator for use in dimethylformamide and other solvents except ethylenediamine. The transition point of azo violet is more on the basic side than thymol blue and is therefore preferable to thymol blue when a very slightly acidic compound is titrated in dimethylformamide or butylamine.

INTERFERENCES

Although a certain amount of water can be tolerated in titrations in 95 to 100% ethylenediamine, excessive amounts should be avoided. Too much water reduces the sharpness of the end point considerably and consequently reduces accuracy.

Water causes high results if present during the titration of salts in dimethylformamide. Amounts as small as 0.5 ml. added during the titration of ammonium nitrate did not affect the sharpness of the end point, but the results were high by as much as 1%. Addition of water during the standardization of the titrant with benzoic acid does not appreciably compensate for this error. A probable explanation is that the ammonia liberated during the titration catalyzes the partial hydrolysis of dimethylformamide to formic acid, which would then be titrated.

The presence of carboxylic acids, enols, phenols, imides, and other acidic compounds will interfere with the determination of salts if present in unknown amounts. Compounds with very reactive halogens may also interfere—for example, the beta-bromine in β-bromoethylamine hydrobromide interferes if the titration is carried out in dimethylformamide or ethylenediamine. If benzene-methanol is used as the solvent this interference is eliminated. Except for the alkali and alkali earth metals, most inorganic cations are sufficiently acidic to interfere.

DISCUSSION

The procedure described was developed to afford maximum convenience and still permit reasonable accuracy. It is estimated that the method as described is accurate and precise to ±0.3%. By using larger samples and larger burets, correcting for volume changes in the titrant due to slight temperature changes, titrating under inert atmosphere to eliminate adsorption of carbon dioxide completely during the titration, purifying all solvents used, calibrating the buret to correct for error of drainage, and correcting for possible salt errors, very great precision and accuracy should be obtained.

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Determination of Sulfa Drugs and Sulfonamides

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The present investigation was prompted chiefly by the lack of an accurate, general method for sulfa drugs. It was found that in basic solvents the acidity of compounds containing the —SO_2NH— group is sufficient to permit titration with 0.1 *N* sodium methoxide in benzene-methanol. Sulfapyridine, sulfadiazine, sulfamerazine, sulfamethazine, sulfathalidine, and sulfathiazole can be titrated in dimethylformamide, giving very sharp end points with thymol blue. Sulfanilamide is not acid to thymol blue in dimethylformamide, but can be titrated in butylamine using *p*-nitrobenzeneazoresorcinol (azo violet) indicator. Sulfaguanidine is not acid in any of the solvents tried. Sulfonamides of thirteen other primary amines were also titrated. The method is rapid and accurate and offers a different avenue of attack from the usual methods for sulfa drugs.

THE present widespread use of sulfa drugs necessitates good analytical methods for their determination. The colorimetric method (*5*) employing diazotization and coupling serves well for small amounts of sulfa drugs. For determination of larger amounts, a volumetric titration of the primary amino group with sodium nitrite using starch–potassium iodide paste as external indicator is widely used, but is lacking in accuracy (*8*) and convenience. Ivanova (*3*) titrated sulfapyridine in acetone solution with sodium hydroxide. Schulek and Rozsa (*7*) applied the well-known bromometric method for aromatic amines to the determination of sulfa drugs, while Laporta and Mossini (*4*) determined sulfapyridine gravimetrically by precipitation with potassium iodobismuthate ($KBiI_4$). In 1948, Tomicek (*10*) published a method for the titration of sulfa drugs as bases in glacial acetic acid. The titrations were carried out potentiometrically because the end points were not sufficiently sharp to permit use of visual indicators; in some cases change in fluorescence in ultraviolet light was used to mark the end point.

The —SO_2NH— group found in sulfa drugs and other sulfonamides of primary amines is known to be feebly acidic. When sulfa drugs are dissolved in basic organic solvents the acidic properties of this group are sufficiently enhanced to permit direct titration with a strong base. This is the basis of the method described. This procedure is simple, rapid, and accurate. Because it involves titration of the —SO_2NH— group, this method is applicable to the determination of sulfathalidine, sulfasuxidine, and other sulfonamides which cannot be analyzed by the diazo method.

REAGENTS AND SOLUTIONS

Butylamine. The commercially available material (Sharples) was used without further purification.

Dimethylformamide (DMF). The commercially available material (Du Pont) was used without further purification.

p-Nitrobenzeneazoresorcinol (azo violet). An approximately saturated solution in benzene.

Sodium methoxide, 0.1 *N*, prepared as described by Fritz and Lisicki (*2*).

Sulfa drugs, U.S.P. grade. The other sulfonamides were prepared in this laboratory according to the procedures of Shriner and Fuson (*9*) and are of 98 to 100% purity.

Thymol blue, 0.3 gram dissolved in 100 ml. of methanol.

PROCEDURE

A sample of suitable size is weighed into a 50-ml. beaker and dissolved in 10 to 20 ml. of dimethylformamide or butylamine. Indicator is added, the beaker is covered with a cardboard provided with a small hole for the buret tip, and the titration is carried out to the first appearance of a clear blue color. During the titration the solution is agitated by means of a magnetic stirrer.

The solvents employed contain some acidic impurities. This is best corrected for by exactly neutralizing the solvent with sodium methoxide shortly before it is to be used.

The sodium methoxide is standardized against benzoic acid using dimethylformamide as solvent and thymol blue as indicator. Titration of benzoic acid in butylamine gives erratic results due to gel formation, but no gel forms in dimethylformamide if 20 to 25 ml. of solvent are used for each 100 mg. of benzoic acid.

SOLVENTS AND INDICATORS

Dimethylformamide is an excellent solvent for sulfonamides. Good end points are obtained for moderately acid sulfonamides using thymol blue indicator. Butylamine enhances the acid strength of sulfonamides more than dimethylformamide and is therefore used for the titration of the more feebly acidic sulfonamides. Azo violet is the preferred indicator for use in butylamine. Butylamine absorbs carbon dioxide more readily than dimethylformamide and is therefore slightly less convenient to use.

SULFA DRUGS

Eight sulfa drugs in common use were analyzed by the above procedure. Sulfaguanidine does not appear to have any acid properties. Sulfanilamide is not acidic to thymol blue in dimethylformamide, but can be accurately titrated in butyl-

Table I. Titration of Sulfa Drugs with Sodium Methoxide

Compound	Sample Wt., Mg.	Base, *N*	Base, Ml.	Purity, %	Solvent	Indicator
Sulfamethazine	153.7	0.0866	6.36	99.6	DMF	Thymol blue
	157.9		6.55	99.9		
	153.7		6.36	99.6		
Sulfamerazine	152.3	0.0866	6.65	99.8	DMF	Thymol blue
	150.6		6.58	99.9		
	152.2		6.64	99.8		
Sulfanilamide	102.3	0.0866	6.84	99.6	$BuNH_2$	Azo violet
	104.1		6.98	99.9		
	101.1		6.76	99.6		
Sulfadiazine	250.0	0.1783	5.57	99.7	DMF	Thymol blue
	250.9		5.60	99.9		
	251.0		5.59	99.7		
Sulfapyridine	124.5	0.1093	4.56	100.1	DMF	Thymol blue
	150.8		5.53	100.2		
	152.5		5.58	100.0		
Sulfathalidine	126.4	0.1093	5.67	98.8	DMF	Thymol blue
	130.3		5.85	98.8		
	126.9		5.70	98.9		
Sulfathiazole	125.6	0.1093	4.51	100.1	DMF	Thymol blue
	127.7		4.59	100.2		
	125.5		4.50	99.9		

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amine using azo violet indicator. In the other drugs the —SO_2-NH— linkage is sufficiently activated by substituent groups to permit titration in dimethylformamide. Table I shows the results of these analyses.

Some differential titrations are possible. Mixtures such as sulfathiazole-sulfanilamide can be analyzed by first titrating sulfathiazole in the presence of sulfanilamide, using dimethylformamide and thymol blue, then titrating both drugs using butylamine and azo violet. The acid sulfa drugs may be accurately determined in the presence of sulfaguanidine. Table II gives data for the analysis of some mixtures.

OTHER SULFONAMIDES

In addition to sulfa drugs the sulfonamides of several primary amines were titrated, in order to determine the scope of the method and to show the effect of substituents on the acidity of sulfonamides. Results are given in Table III.

p-Toluenesulfonamide is slightly acid and gives a good end point in butylamine but not in dimethylformamide. Substitution of one hydrogen by a phenyl group ($PhSO_2NHPh$) increases the acidity sufficiently to permit titration in dimethylformamide. This is probably due to the tendency of a phenyl group to attract electrons. The electron-donating properties of an alkyl group, however (as in $PhSO_2NHR$), weaken the acidity so that a poor end point is obtained on titration in butylamine. From the titrations carried out it appears that the order of acidity is: $ArSO_2NHPh$, $ArSO_2NHPyr$, $ArSO_2NH$thiazole > $ArSO_2NH_2$, $ArSO_2NH$naph > $ArSO_2NHCH_2Ph$ > $ArSO_2NHR$ > $NaphSO_2NHR$. A detailed study of acidity of the more acidic sulfonamides has been made by Bell and Roblin (*1*).

The presence of the phenolic group in *p*-$HOC_6H_4NHSO_2C_6H_4Br$ caused no interference in dimethylformamide, except that a slight green color formed shortly before the end point. In butylamine using azo violet indicator, the acidity of the phenolic group is sufficiently enhanced to interfere with the end point.

DISCUSSION

For the compounds in which a poor end point was observed in butylamine and dimethylformamide, a somewhat sharper end point was obtained in 95 to 100% ethylenediamine. Because of lack of adequate supply of this solvent in this laboratory, further investigation was discontinued.

In the identification of organic amines, sulfonamides are among the commonly used derivatives. It is suggested that titration of the sulfonamides be used in the determination of the equivalent weight of primary amines. By observing the sharpness of the end points in each of the two solvents recommended, knowledge of the basic strength and character of the parent amine may be obtained.

Methods have recently been suggested for the potentiometric titration of weak acids in basic solvents (*2*, *6*). Use of potentiometric methods would undoubtedly permit a more delicate determination of the effect of substituents on the acid strength of

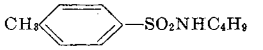
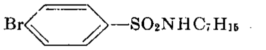
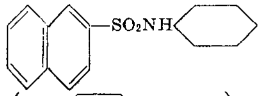
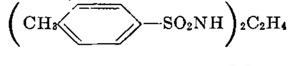
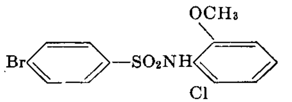
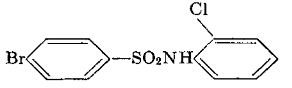
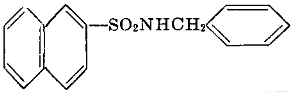
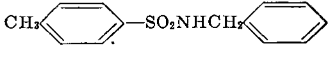
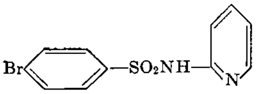
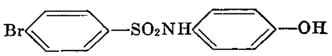
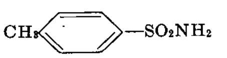
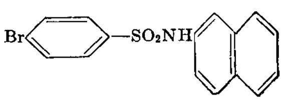
Table II. Titration of Sulfonamide Mixtures

Sulfapyridine Taken, Mg.	Base, Ml.	Base, *N*	Found, %
Sulfaguanidine (0.2 gram) added as impurity. DMF solvent, thymol blue indicator			
173.5	4.70	0.1477	100.0
183.3	4.97	0.1477	100.0
Sulfanilamide (0.2 gram) added as impurity. DMF solvent, thymol blue indicator			
Sulfathiazole, Mg.			
181.7	4.82	0.1477	99.9

Butylamine solvent, azo violet indicator

Sulfanilamide, Me.	Sulfathiazole, Me.			Total Taken, Me.	Total Found, Me.
0.413	0.396	5.57	0.1477	0.810	0.823
0.418	0.399	5.61	0.1477	0.817	0.828
0.412	0.422	5.62	0.1477	0.829	0.829

Table III. Titration of Sulfonamides of Some Primary Amines

Compound	Solvent	Indicator	Purity
	$BuNH_2$	Azo violet	100.7 101.3 100.8
	$BuNH_2$	Azo violet	100.4 100.1 101.9
	$BuNH_2$	Azo violet	99.8 98.2 97.3
	$BuNH_2$	Azo violet	98.6 98.6 98.9
	$BuNH_2$ + DMF	Azo violet	96.3 96.7 96.9
	$BuNH_2$	Azo violet	99.6 99.8
	DMF	Thymol blue	98.1 98.1 98.0
	$BuNH_2$	Azo violet	97.8 97.8 97.8
	$BuNH_2$	Azo violet	99.6 99.6 99.7
	DMF	Thymol blue	100.2 100.0 100.2
	DMF	Thymol blue	98.7 98.8 98.8
	$BuNH_2$	Azo violet	100.0 100.1 100.0
	$BuNH_2$	Azo violet	100.0 100.0

sulfonamides. The reliability of such potentiometric curves has as yet, however, not been convincingly demonstrated.

ACKNOWLEDGMENT

The authors wish to acknowledge gratefully the assistance of Lewis J. Throop who helped prepare some of the sulfonamides used in this work.

They also wish to thank the R. P. Scherer Co., Gelatin Products Division, for supplying some of the sulfa drugs and E. I. du Pont de Nemours & Co., which donated the dimethylformamide used.

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RECEIVED January 22, 1951.

Round-Table Discussion

Titrations in Nonaqueous Solutions

Moderator: JOHN A. RIDDICK, ***Commercial Solvents Corp., Terre Haute, Ind.***
Panel: JAMES S. FRITZ[1], ***Wayne University, Detroit, Mich.***
MARION MACLEAN DAVIS, ***National Bureau of Standards, Washington, D. C.***
E. F. HILLENBRAND, JR., ***Carbide and Carbon Chemicals Corp., South Charleston, W. Va.***
P. C. MARKUNAS[2], ***Commercial Solvents Corp., Terre Haute, Ind.***

THE round table discussion of titrations in nonaqueous solvents gave a resume of the present status. The following topics were discussed by the several panel members: solvents and titrants, indicators, applications, accuracy, precision, interference, and limitations.

SOLVENTS AND TITRANTS

The general requirements for solvents to be used for titration in nonaqueous solvents are fairly simple.

1. The first one is fairly obvious: The solvent must be available at a reasonable price. There are probably many solvents that are superior in certain respects, but they are not available commercially at a reasonable price.
2. A solvent must dissolve the substance being titrated or the substance must dissolve when excess titrant is added. An excess of the titrant may be back-titrated as in aqueous systems.
3. The products of titration preferably should be soluble, and if a precipitate is formed it should be dense and crystalline and not gelatinous.
4. The solvent should not enter into side reactions.
5. The solvent should be such that the titration can be followed potentiometrically. There are no electrode systems available which are satisfactory for following the reaction in solvents that have low dielectric constants. The behavior of the electrodes in nonaqueous systems needs a considerable amount of investigation.

The requirements for titrants are about the same as for those in aqueous systems. They should react rapidly and quantitatively, with no side reactions with the substance being analyzed or with the solvent. They should be stable on standing without any appreciable change in the titer or the development of color.

There are three types of titrations in aqueous solutions which also can be carried out in nonaqueous solutions. The first general type is the redox reaction. Only a few known redox analytical methods take place in nonaqueous solvents. Not much work has been done in this field. The second type is volumetric precipitation and complex-forming reactions. Practically nothing has been done in strictly nonaqueous systems. The third general type is acid-base titrations. Today this is the most important field because more work has been done to show the possibilities.

If a base such as an aliphatic amine is fairly strong, it can be titrated satisfactorily in aqueous solution. Weaker bases, such as the pyridine type or aromatic amines, will not give a satisfactory end point in water. The bases that are too weak to be titrated in water become much stronger bases when dissolved in such solvents as acetic acid. The strong acids in water—hydrochloric, nitric, sulfuric, perchloric, etc.—show decidedly different strengths in nonaqueous solutions. Perchloric acid is the strongest known acid in acetic acid. Many compounds of different chemical types may be titrated in acetic acid using the titrant perchloric acid dissolved in acetic acid. In some instances, a substance that cannot be titrated satisfactorily by a titrant dissolved in the same solvent as the sample can be titrated if the titrant is dissolved in a different solvent. For example, hexamethylenetetramine cannot be titrated in acetic acid with perchloric acid dissolved in acetic acid, but if the perchloric acid is dissolved in *p*-dioxane the titration is satisfactory.

The strength of weak acids is increased in solvents which have almost no acidic character or whose properties are basic. The titrant should be a strong base in the solvent system used. Two solvents have been proposed which exhibit outstanding properties for titration of substances that show extremely weak acidic properties in water, such as phenols: ethylenediamine and dimethylformamide. No satisfactory indicator has been reported for ethylenediamine.

The relative value of some of the titrants that have been proposed was discussed.

INDICATORS

Indicators were defined for this discussion to include electreod systems and organic compounds that change color at definite acidities or basicities. In general, the electrode systems are the same as those used in water. Two years ago it was reported that conductometric titrations were superior to potentiometric at least for fatty acids in soap mixtures. The most common electrode system in use today is the glass-calomel. The glass-antimony electrodes have been found most satisfactory for amine solvents. It seems likely that high frequency titrations may expand in the field of titration in organic solvents.

The organic compounds used as indicators are in general the ones that have been found suitable for use in water. Others have been reported, and there are many that appear to be promising in a group used as biological stains. A large percentage of the indicators that have found use belong to the triphenylmethane group. The remaining ones belong to various group types and do not find

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too wide an application. The remainder of the discussion was very informative and concerned the theory of triphenylmethane indicators and their application to acid-base titrations in the several solvent systems.

APPLICATIONS

The applications were limited to acid-base titrations. They are divided into two parts: the determination of substances that behave as bases in acidic solvents, and those that behave as acids in basic solvents.

The substances that act as bases in acidic solvents can be divided into three general classes: primary, secondary, and tertiary amines; amine salts of carboxylic acids; and metallic salts of carboxylic acids. Nadeau and Branchen demonstrated the titration of amino acids in acetic acid with 0.1 *N* perchloric acid in acetic acid. Blumrich and Bandel determined tertiary amines in a mixture of amines by acetylating the primary and secondary amines and titrating the unacetylated tertiary amine in acetic acid. Markunas and Riddick developed a method for the determination of choline salts in aqueous solutions.

Pifer and Wollish have made an extensive study of the determination of amine, heterocyclic, and quaternary ammonium salts. They have extended the application of titration in nonaqueous solutions to include chlorides of these salts.

The fact that amine salts may be titrated in nonaqueous solutions has led to a number of important applications. For instance, acid anhydrides can be determined by reaction with a measured excess of morpholine. Epoxy compounds may be determined in a similar manner by using different solvents and titrants. Moss, Elliott, and Hall have shown that salicylic acid may be titrated in ethylenediamine. Katz has modified and adapted their method for the determination of acidic products of catalytic reactions, particularly for phenolic-type compounds. This procedure has formed the basis of a method for determining primary amines. The method has not been successfully applied for the determination of aromatic amines or ethanolamines. The combination of direct titration and titration of reaction products has been made the basis for determination of mixture of acetic acid and acetic anhydrides.

ACCURACY, PRECISION, INTERFERENCES, AND LIMITATIONS

The precision, or reproducibility of results, and the accuracy are on the same order as for acid-base titrations in aqueous solutions. The accuracy was established by using primary standards such as potassium acid phthalate, sodium carbonate, and diphenylguanidine. A standardization of the titrant by two or more standards can be made as accurately as in aqueous solutions. The analysis of highly purified substances with a titrant standardized by one of the accepted standards approached 100% within the accuracy of the method. Titrations using the best technique will agree to ±0.05%. The accuracy and precision have been demonstrated by several workers in the field.

Some of the major limitations are large volume changes in the titrant due to temperature changes, insolubility of sample in solvent, lack of variety of indicators, and unpredictable reactions of some samples with the titrant and the solvent. In a survey of the application of titration in acetic acid with perchloric acid in acetic acid as the titrant it was found that about 10% of approximately 600 compounds tested were insoluble in acetic acid. Some methods were prescribed for overcoming the insolubility difficulty.

One of the substances causing the most interference is water. The water may be eliminated in most samples by the addition of acetic anhydride. However, some substances react with acetic anhydride, and to date no method has been devised to eliminate the effect of water present in such materials.

There have been several anomalous behaviors reported when titrating in nonaqueous solvents. A few of these were cited.

REMARKS

In the discussion following the panel presentation it was brought out that acid-base reactions in nonaqueous solvents are not classified as such in *Chemical Abstracts*. This makes it difficult to survey the literature on the subject. The moderator was requested to confer with E. J. Crane to determine whether or not it would be feasible to have nonaqueous titrations listed separately in the subject index of *Chemical Abstracts*.

Considerable time was devoted to the discussion of possible indicators. Davis explained the line of work that she and her coworkers were pursuing at the National Bureau of Standards. She gave some excellent suggestions for additional investigation on indicators.

The application of nonaqueous titrations as a control procedure in plant operation and as a means for analyzing the finished product was discussed. Three companies have adopted the use of titration in nonaqueous solvents and have found that they have been able to analyze certain products much more readily. In some cases the cost of analysis has been greatly reduced.

ACKNOWLEDGMENT

The moderator wishes to express his appreciation to H. H. Willard for his assistance and advice in organizing this round table. It was a pleasure to have N. F. Hall present.

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[END OF TITRATIONS SERIES]

Titrimetry in Glacial Acetic Acid

Determination of Choline Salts of Carboxylic Acids

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The purpose of this study was to develop a rapid and accurate method for the determination of choline salts of carboxylic acids. The choline salt is dissolved in glacial acetic acid and titrated with perchloric acid in acetic acid. By a slight modification, the method was also adapted to the aqueous solutions of these choline salts. The method is as precise and accurate as aqueous acidimetric procedures and when applied to the analysis of production samples seems to have no error in excess of ±0.2%. Both dry and aqueous solutions and purified and technical choline carboxylic acid salts may be analyzed. The method has proved a most convenient and rapid means of process control and analysis.

TWO accurate gravimetric methods for the determination of choline salts have recently been proposed. One is based upon the formation of an ethanol-insoluble complex compound of choline chloride and cadmium chloride, $(CH_3)_3NCl.C_2H_5OH.CdCl_2$ (*6*). The other is based upon the precipitation of choline as the reineckate (*4*). The latter has an advantage over the former in that the choline may be precipitated from an aqueous solution. However, both methods have the disadvantage inherent in gravimetric procedures—they are time-consuming in comparison to volumetric procedures.

In a preliminary survey of the usefulness of a proposed technique employing titrimetry in glacial acetic acid for the analysis of carboxylic acid salts and weak bases, it was shown that choline dihydrogen citrate can be determined by titration with perchloric acid in glacial acetic acid (*3*). The survey, however, was limited to the testing of compounds of highest purity commercially available and no effort was made to apply the method to the determination of any particular compound nor to demonstrate its usefulness in production control or in the analysis of mixtures.

This titrimetric method has now been applied to the determination of choline gluconate, choline dihydrogen citrate, and choline hydrogen tartrate in purified and technical grade preparations and to aqueous solutions of these choline salts. From data obtained during the preliminary survey, it is concluded that the method is applicable also to the determination of other carboxylic acid salts of choline, but not to choline chloride. This latter compound, however, can be determined by the recently proposed procedure of Pifer and Wollish (*5*).

REAGENTS AND APPARATUS

The reagents and apparatus used were those outlined in the original paper (*3*), except for the choline salts.

Choline dihydrogen citrate was purified by recrystallization from a mixture containing equal volumes of ethanol and methanol and dried in a vacuum oven at room temperature.

Choline gluconate solution was prepared by adding about 5% excess of gluconic acid to an aqueous solution of choline base and removing part of the water at reduced pressure.

Choline bicarbonate solution was prepared by passing carbon dioxide into an aqueous solution of the free choline base.

Choline hydrogen tartrate was prepared by adding a 2% excess of tartaric acid to a solution of choline bicarbonate and removing all the water under vacuum.

The choline dihydrogen citrate, gluconate, and bicarbonate were found to contain less than 0.05% trimethylamine.

Sample Solution of Choline Dihydrogen Citrate. About 46 grams of choline dihydrogen citrate, accurately weighed, were dissolved in glacial acetic and transferred quantitatively to a 1-liter volumetric flask. The solution was allowed to reach room temperature, and made to volume.

PROCEDURE

Potentiometric Titration, Method I. A sample containing about 3.5 milliequivalents of salt is accurately weighed into a tall-form beaker, without spout, dissolved in 30 ml. of glacial acetic acid, warmed if necessary to effect solution, cooled to room temperature, and titrated potentiometrically with 0.1 *N* perchloric acid in acetic acid. The titration is conducted and the equivalence point determined in the manner employed for a potentiometric titration in aqueous solution.

Indicator Titration, Method II. The same weight of sample as required for the potentiometric method is accurately weighed into a 250-ml. Erlenmeyer flask and dissolved in 30 ml. of acetic acid. One drop of crystal violet indicator is added and the solution is titrated to a blue-green color with the 0.1 *N* perchloric acid solution.

EXPERIMENTAL

Precision and Accuracy. A sample of recrystallized choline dihydrogen citrate analyzed by the procedure outlined in Method II gave the following values: 99.92, 99.87, 100.04, 99.99, 100.05, and 100.05; average 99.98%. The same sample analyzed by the potentiometric procedure, Method I, gave values of 100.03, 100.05, 99.91, 99:94, and 99.95; an average of 99.98%. The mean deviation for the replicate values for choline dihydrogen citrate by Method I is ±0.05% and by Method II is ±0.06%.

Table I. Effect of Water on Assay of Choline Dihydrogen Citrate

Sample Solution	Water Added	Approximate Water Content of Sample[a]	Choline Dihydrogen Citrate Found
	Ml.	%	%
1	0.0	0	99.98, 100.00
2	0.1	10	99.95, 99.95
3	0.2	15	99.95, 99.98
4	0.4	26	100.03, 100.00
5	0.8	41	100.46, 100.46
6	1.6	58	101.85, 101.85
7	2.0	63	102.66, 102.69

[a] Calculated from weight of sample introduced (in 25 ml. of sample solution) and water added.

Interferences. Ethyl acetate, ethyl ether, acetonitrile, acetone, *p*-dioxane, nitromethane, benzene, petroleum ether, and carbon tetrachloride do not interfere with the titration of choline salts of carboxylic acids when any of these compounds comprise as much as 10% by volume of the original solvent. The effect of larger amounts of these solvents was not determined. However, no interference is expected, as it was recently shown that many of these reagents can be used in nonaqueous titrimetry (*2*). The presence of either ethanol or methanol in the solvent or sample appears to decrease slightly the basicity of choline salts in glacial acetic acid but otherwise does not interfere with the assay.

Trimethylammonium carboxylic acid salts, if present in the choline preparation, will be titrated and determined as the choline salt. This is not a serious interference because it is possi-

Table II. Determination of Choline Dihydrogen Citrate in Presence of Water

Solution	Water Added	Approximate Water Content of Sample	Choline Dihydrogen Citrate Found, % Indicator End Point	Choline Dihydrogen Citrate Found, % Potentiometric End Point
	Ml.	%		
1	0.0	0	...	99.95
2	0.1	10	...	100.08
3	0.2	15	...	100.06
4	0.4	26	99.86	99.81
5	0.8	41	99.86	99.95
6	1.6	58	99.86	100.03
7	2.0	63	99.83	99.81

ble to correct for presence of the trimethylammonium salt after determining its content by a recently developed method (*1*).

Small amounts of water have no detectable effect upon the determination of choline carboxylic acid salts, but large amounts of water give high results. The magnitude of this effect is indicated by the values in Table I.

Determination of Choline Salts in Presence of Water. By a slight modification of the described procedure it is possible to assay accurately samples of choline salts containing as much as 90% water. This modification, designated Method III, consists of adding sufficient acetic anhydride to the sample in acetic acid to react with the water introduced with the sample, very gently boiling the mixture for 5 minutes, cooling to room temperature, and titrating with the 0.1 *N* perchloric acid solution, using either the indicator or potentiometric procedure to obtain the end point.

When Method III was applied to a number of 25-ml. aliquots of the sample solution to which known amounts of water were added, the values shown in Table II were obtained.

An approximately 50% aqueous solution of choline bicarbonate analyzed by an aqueous acidimetric procedure gave values of 49.49, 49.49, 49.46, 49.43, 49.40, and 49.44; average 49.45%. When this sample was analyzed by Method III, employing an indicator end point, the results obtained were: 49.38, 49.38, 49.44, 49.45, 49.42, and 49.43; average 49.42%. These values not only indicate the high precision and accuracy of Method III but also substantiate the fact that the described nonaqueous titrimetric procedure is as precise and accurate as aqueous acidimetric and alkalimetric methods.

Application. A sample of choline hydrogen tartrate which had a moisture content of 1.00% (by the Karl Fischer method) and free tartaric acid content of 1.95% was assayed by Method I. An average value of 96.91% was obtained.

A production sample of choline gluconate, manufactured to contain very close to 62.5% choline gluconate, assayed by Method III (indicator end point) gave replicate values of 62.15, 62.14, 62.09, 62.12, 62.04, 62.00, 62.09, 62.11, and 62.07; average 62.09%. This sample had free gluconic acid and moisture contents of 5.1 and 32.9%, respectively.

These two examples illustrate the applicability of the described methods to the analysis of production samples of choline carboxylic acid salts and demonstrate that the proposed procedures seem to have no error in excess of ±0.2%.

DISCUSSION

When aqueous solutions of choline dihydrogen citrate or choline hydrogen tartrate are analyzed by Method III, slightly lower results are obtained by the indicator than by the potentiometric end-point procedure. This is due to the slight obscuring of the indicator end point by darkening (browning) of the solution during the refluxing period. The discoloration does not interfere with the assay, and after a few trials the end point can be duplicated without difficulty. The discoloration does not occur with choline gluconate or bicarbonate.

The amount of acetic anhydride added in Method III is not critical. Excess acetic anhydride does not interfere with the determination and equally good results can be obtained if only enough anhydride is added to react with 80 to 90% of the water introduced with the sample.

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Fatty Amine Products of High Molecular Weight

Quantitative Titration in Acetic Acid

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AQUEOUS titrimetry appears adequate for the fatty primary amines of high molecular weight. However, it has been found of little or no value when applied to the acetates of the fatty primary amines, which are commercial products useful in ore beneficiation; and certain secondary and tertiary amines of high molecular weight. This paper concerns the adaptability of titrimetry in glacial acetic acid to diverse fatty amine products of high molecular weight.

Conant and Hall (*3*) in their study of "superacid solutions" found that many organic compounds behave as strong bases in glacial acetic acid whereas they show no basic property in water. In view of the acid-base relationships which exist in glacial acetic acid (*1, 3–5, 7, 8, 11*), it appeared probable that these fatty amine products could be quantitatively titrated in glacial acetic acid with perchloric acid. Accordingly, different compounds such as the fatty primary amine acetates, fatty secondary amines, mixed tertiary amines, fatty aminonitriles—for example, *N*-alkyl-β-aminopropionitriles—and fatty materials containing both primary and secondary amino groups—for example, *N*-alkyl-γ-aminopropylamines—were tested. In the present study, it was found that glacial acetic acid was an excellent solvent for all the fatty amine products tested and perchloric acid was a highly satisfactory titrant.

REAGENTS AND SOLUTIONS

Perchloric acid, 70 to 72%, ACS grade
Acetic anhydride, ACS grade

Because conventional aqueous titrimetry methods are not applicable for a number of fatty amine products of high molecular weight, such as fatty amine acetates, fatty secondary and tertiary amines, and fatty aminonitriles, it was desirable to develop a method for titrimetric determination of diverse fatty amine products. The use of perchloric acid as titrant in glacial acetic acid as solvent gives excellent results with a wide variety of fatty amine products including the primary, secondary, and tertiary fatty amines and their acetates, as well as fatty amino nitriles and compounds containing both primary and secondary amino groups. The method makes possible the rapid and accurate determination of a large number of fatty amino compounds which cannot be titrated by the conventional aqueous method.

Acetic acid, glacial, ACS grade

Perchloric acid solution, 0.1 *N*

The standard acid solution is prepared by adding 14.2 grams of the perchloric acid reagent to 500 ml. of glacial acetic acid; acetic anhydride (23.3 grams) is added with stirring and the solution is then made up to 1000 ml. by dilution to the mark with more glacial acetic acid. The solution is standardized against anhydrous sodium carbonate (AR grade material is heated to 350° C. for 2 hours) to the crystal violet end point. Acid potassium phthalate NBS has been recommended as the primary standard (*10*).

Crystal violet indicator, 1 gram of crystal violet dissolved in 100 ml. of glacial acetic acid.

Table I. Representative Fatty Amine Products

Fatty Amine Product	Amine Number	
	Theory	Found
Octadecylamine	208.2	208.0
Hexadecylamine	232.4	233.7
Oleyl amine[a]	209.8	209.0
Dioctadecylamine	107.5	107.8
N-Methyldioctadecylamine	104.7	105.0
Octadecylamine acetate[b]	170.3	170.3
N-Dodecyl-β-aminopropionitrile	235.3	235.6
N-Octadecyl-γ-aminopropylamine	343.6	342.0
N-Dodecylaminoacetonitrile	250.0	249.5
N-Dodecyl-β-aminoethylamine	491.3	486.3

[a] Iodine value, theory 95.5, found 96.1.

[b] Prepared from 99% octadecylamine by addition of requisite quantity of glacial acetic acid.

ANALYTICAL PROCEDURES

The fatty amine product (0.5 to 1.0 gram) is weighed accurately into a 200-ml. Erlenmeyer flask and dissolved in 50 ml. of glacial acetic acid by gentle warming. One drop of the crystal violet indicator is added and the warm solution is titrated with 0.1 *N* perchloric acid in acetic acid to a green color [solutions are maintained at a slightly elevated temperature (30° to 45° C.) in order to avoid the precipitation of the perchloric salts].

CALCULATION

$$\text{Amine No.} = \frac{\text{ml. of } 0.1\ N \text{ acid} \times N \times 56.11}{\text{sample weight}}$$

The amine number may be defined as the number of milligrams of potassium hydroxide which is equivalent to 1 gram of the amine product.

EXPERIMENTAL

The primary and secondary fatty amines were prepared by the catalytic hydrogenation of the corresponding nitriles. The *N*-methyldialkyl amines were prepared from the secondary fatty amines by the formaldehyde-formic acid procedure (*2*). The reaction between acrylonitrile and the fatty amines yielded the *N*-alkyl-β-aminopropionitriles which were converted to the *N*-alkyl-γ-aminopropylamines (*6*). The *N*-alkylaminoacetonitriles were prepared by the reaction of the fatty amines with sodium cyanide, formaldehyde, and sodium bisulfite (*9*). Reduction of the substituted acetonitriles with lithium aluminum hydride gave the *N*-alkyl-β-aminoethylamines. All the above products were highly purified by distillation and crystallization procedures. The results of the analyses of a number of representative fatty amine products are summarized in Table I.

DISCUSSION

Whereas aqueous titrimetry is satisfactory for the fatty primary amines, it gives erratic results with some fatty secondary amines because of solubility factors and is of little or no value when applied to the *N*-methyldialkyl amines, fatty tertiary amines, fatty amine acetates, and *N*-alkylaminoacetonitriles. In Table I, the octadecylamine acetate is given as the representative example of an acetate of a fatty amine product. However, the acetates (either mono- or di-) of the other products were also prepared and tested. The colorimetric titration with perchloric acid in acetic acid was highly satisfactory for all the acetate materials.

The data presented in Table I clearly demonstrate the versatility and accuracy of the nonaqueous method and its applicability to diverse fatty amine products.

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Infrared Spectra of Steroids

New Solvents for Steroids Difficultly Soluble in Carbon Disulfide

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In studies of the infrared spectra of certain highly purified steroids from 2 to 15 microns (5000 to 666 cm.$^{-1}$), difficulty is frequently encountered in obtaining spectra suitable for comparison purposes. These steroids are often only slightly soluble in the usual nonpolar solvents. Two approaches have resulted in some success in overcoming this difficulty; 0.2% solutions of Δ^5-pregnene-3(β)-ol-20-one in carbon disulfide yielded suitable fingerprint region spectra in a cell of long path length (8.5 mm.). Stabilized polar liquids with heavy atoms in their molecular structure were investigated in an effort to find solvents that would produce little or no interference in the spectra. The spectra of purified bromoform and methylene bromide in 0.2- and 1-mm. cells are shown together with 17-ethinylestradiol in bromoform and 16,17 (α)-oxido-Δ^5-pregnene-3(β)-ol-20-one in methylene bromide solutions. Purified bromoform and methylene bromide were found to be good solvents for these steroids and yielded fingerprint spectra far superior to chloroform and carbon tetrachloride. By supplementing spectra in bromoform with those in methylene bromide only narrow regions of the spectrum remain unavailable. Both solvents produce no interference in the double bond region where carbon disulfide is not usable.

AMONG the difficulties in the infrared spectrometry of solids may be included the problems of preparing sufficiently thin films (*9*), loss of energy from the beam through scattering by crystalline samples (*2, 4, 11, 19, 22*), and spectral variations due to partial sample orientation and possible polymorphism (*1*). Although mulling with mineral oil or perfluorokerosene has been used to reduce scattering losses, it has been the experience of this laboratory that interpretations of solid spectra, particularly those of steroids, are frequently questionable because of the above effects, the impossibility of reproducing exactly the amount of sample in the beam, and concurrent resolution differences. The presence of absorption band differences between several samples of the same compound in mineral oil mull spectra, which were absent when spectra of the same samples were determined in solution, has been attributed to polymorphism (*12, 17*).

Solution spectra, although more reliable in interpretation, are complicated by the existence of relatively few solvents which do not absorb throughout large intervals of the 2 to 15 micron (5000 to 666 cm.$^{-1}$) region (*20*). The use of solvent-filled compensation cells in the reference beam of double-beam infrared spectrometers can reduce interferences from less intense solvent absorption bands, but is of no value when absorption is so great as to render the instrument inoperative (*21*). A suitable solvent for infrared spectrometry should have a spectrum relatively free from absorption bands and a fair degree of stability, should not react with the sample or the materials of the absorption cell, and must dissolve enough solute to give absorption bands of satisfactory intensity in the fingerprint region of the spectrum. For steroid samples, approximately 1 to 3% solutions in sodium chloride cells of 1-mm. path length are required (*7*). Carbon disulfide, carbon tetrachloride, and chloroform (*3, 13, 15, 20*) are the solvents most frequently used. Carbon disulfide has by far the fewest absorption bands, but many steroids, particularly those with several hydroxyl groups, cannot be dissolved to a sufficiently great extent to yield satisfactory spectra (*16*). Similarly, carbon tetrachloride is a poor solvent for many steroids and in addition absorbs so strongly from 7.8 to 15 microns (1280 to 666 cm.$^{-1}$) as to preclude obtaining satisfactory spectra in the fingerprint region. Chloroform has been used frequently in steroid studies (*14*) and will usually dissolve sufficient sample. Unfortunately, the

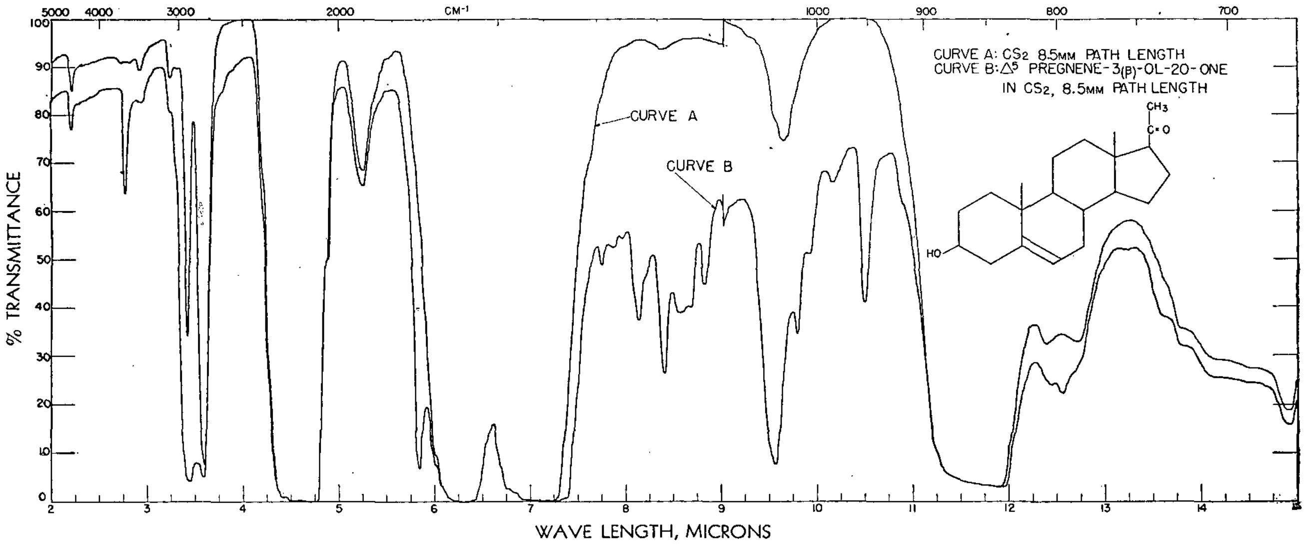

Figure 1. Δ^5-Pregnene-3(β)ol-20-one in Carbon Disulfide

3 mg. per ml.

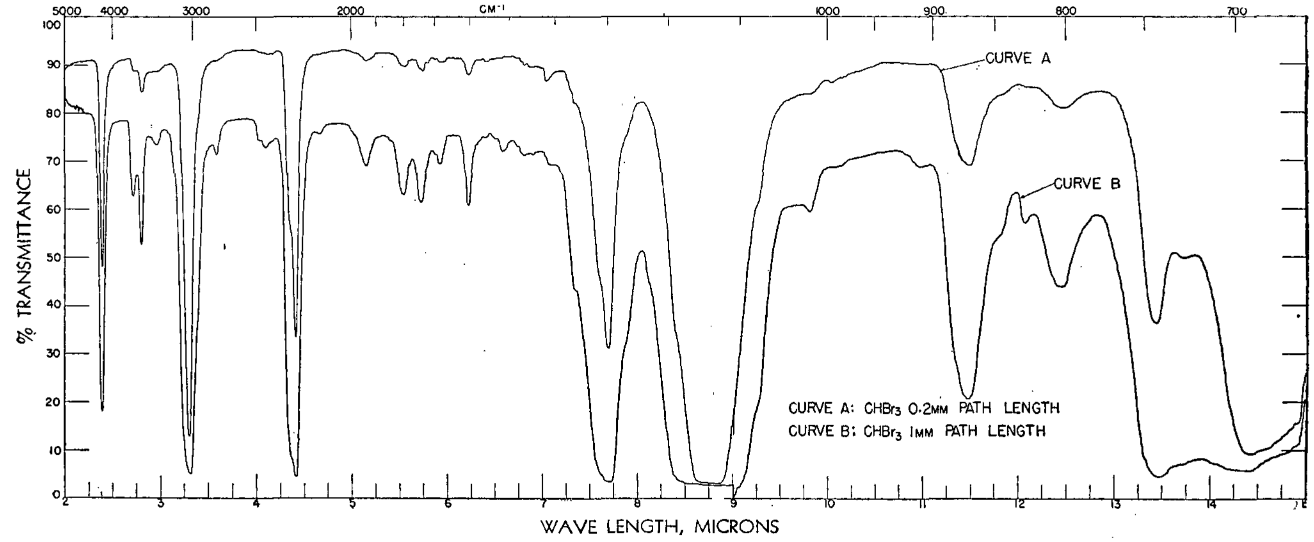

Figure 2. Bromoform in 0.2-Mm. and 1-Mm. Path Lengths

multiplicity of absorption bands permits only scattered observation in the fingerprint region (*6*, *16*) and in addition masks portions of the functional group region.

During the past year, two approaches in these laboratories have found some success in overcoming the above difficulties. An absorption cell of 8.5-mm. path length was prepared by soldering (*10*) sodium chloride windows to a brass spacer. It is thus possible to introduce 8.5 times as much sample into the infrared beam as with conventional 1-mm. cells. With relatively insoluble samples, such as highly purified Δ^5-pregnene-3(β)-ol-20-one, suitable spectra in the fingerprint region were obtained (Figure 1), although a concentration of only 0.2% in carbon disulfide could be prepared. There is some broadening of the major carbon disulfide absorption bands, as well as increased interference from the smaller bands. Minor variations in purity of carbon disulfide are more apparent at this path length and make it advisable to determine a solvent reference spectrum on each new shipment.

Theoretical considerations (*2*, *19*), as well as published spectra (*5*, *8*, *18*), suggest that the replacement of chlorine in halogenated methanes by heavier elements (leading to displacement of the carbon-halogen absorption bands to longer wave length) might result in good solvents with fewer interferences in the 2 to 15 micron (5000 to 666 cm.$^{-1}$) region. In preliminary studies, methylene iodide was considered but soon proved to be unstable. Freshly distilled methylene iodide discolored rapidly and gave many absorption bands. Both redistilled bromoform (Figure 2) and methylene bromide (Figure 3) were found to give suitable spectra in cells of 0.2- and 1-mm. path length. In general, the solubility of steroids in these solvents parallels that in the corresponding chlorinated solvents, a tremendous increase over that in carbon disulfide and carbon tetrachloride. Bromoform is the preferred solvent, as it causes less interference than methylene bromide in the functional group region, and there is no interference in the region around 8 microns, frequently needed for confirmation of the presence of $-\overset{\|}{C}-O-C-$ of acetate groups. By recourse to spectra in methylene bromide as well as in bromoform (0.2-mm. path length), only the narrow regions of the spectrum—2.40 to 2.45 microns (4170 to 4070 cm.$^{-1}$), 3.25 to 3.40 microns (3070 to 2940 cm.$^{-1}$), 8.40 to 8.70 microns (1190 to 1149 cm.$^{-1}$), and 14.8 to 15.0 microns (676 to 666 cm.$^{-1}$)—remain unavailable. The spectra of 17-ethinylestradiol and 16,17(α)-oxido-Δ^5-pregnene-3(β)ol-20-one (Figures 4 and 5) are typical results. Correla-

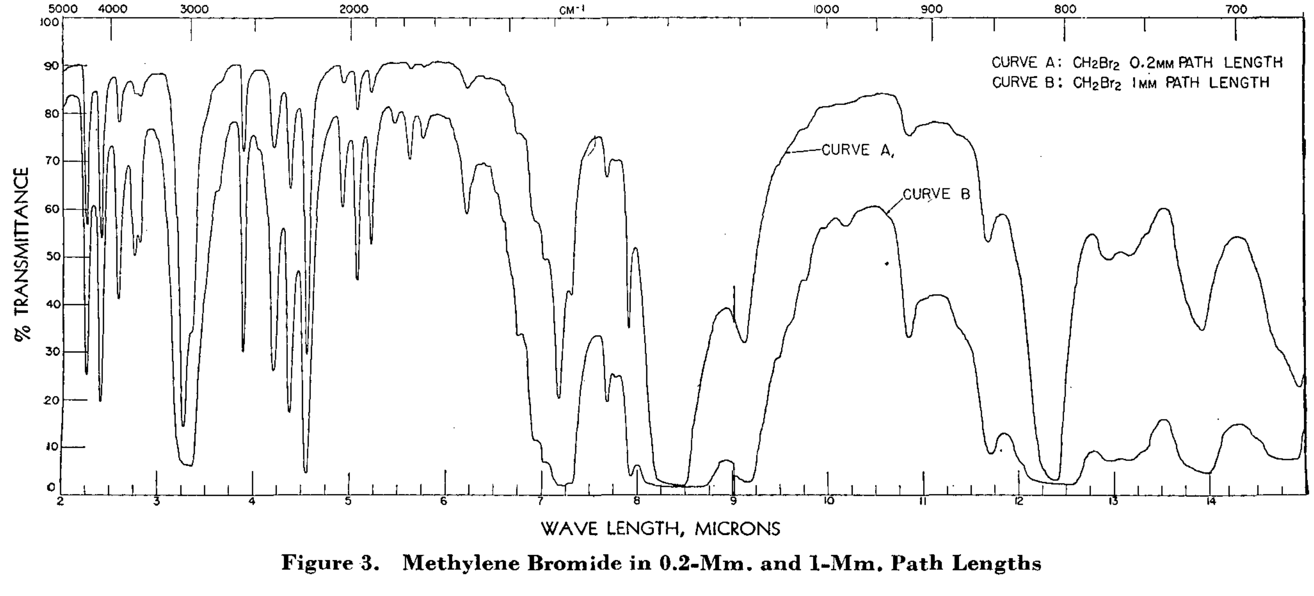

Figure 3. Methylene Bromide in 0.2-Mm. and 1-Mm. Path Lengths

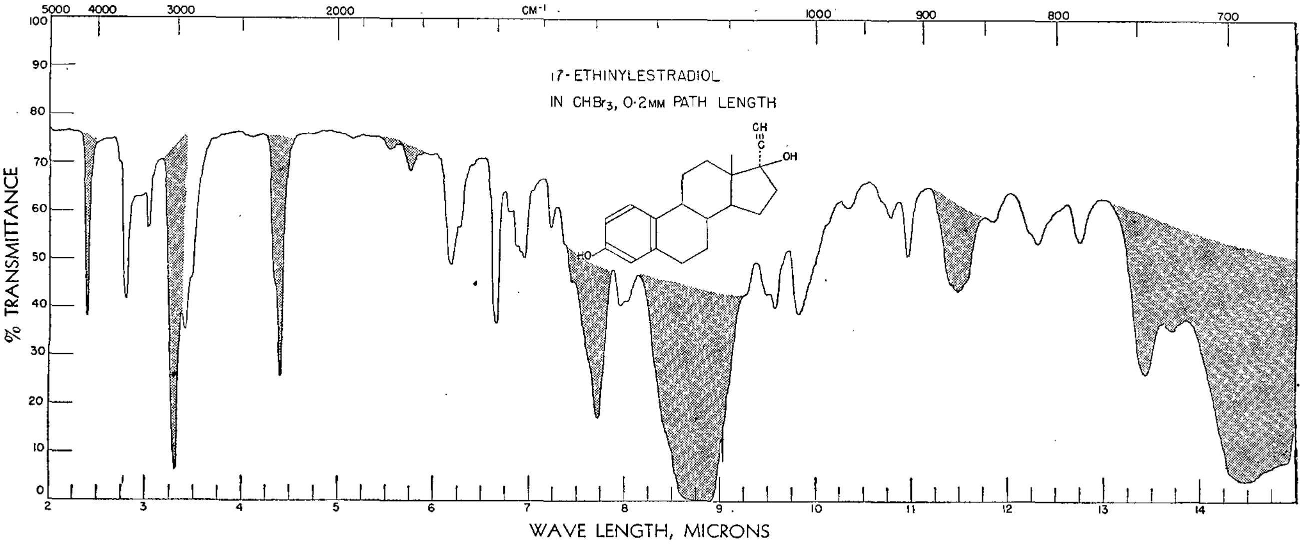

Figure 4. 17-Ethinylestradiol in Bromoform

30 mg. per ml.

tions of absorption band wave length with structure using chloroform as a solvent appear to apply without shift to bromoform and methylene bromide. Similarly, resolution of adjacent bands seems not to have been affected.

EXPERIMENTAL

Determination of Infrared Spectra. A Perkin-Elmer Model 12C single-beam spectrometer with sodium chloride prism was used in the early phases of this work. More recently a Perkin-Elmer Model 21, double-beam spectrometer was used. No attempt was made to compensate for solvent absorption bands, but the absorption bands of carbon dioxide, and water vapor in the air, are automatically compensated in the latter instrument. All spectra were run under conditions usual in this laboratory for survey studies. Solute concentration and path length of the cell are indicated on the spectra. About 25 minutes were taken to record each spectrum using an intermediate rate of response of the balancing and recording system. The scanning speed was automatically reduced when sharp absorption bands were recorded.

Bromoform. In order to obtain bromoform of sufficient spectral purity, ethyl alcohol and other impurities must be removed. Bromoform (Merck or Baker U.S.P.) was fractionated under vacuum (25 mm. of mercury) in a 50-cm. all-glass Snyder column and the forerun of 30% was discarded. The main fraction, 60% (boiling point 49–50° C., 25 mm. of mercury), was collected while the colored residue amounting to 10% was discarded. The usable main fraction was stored in small brown glass bottles, so that only enough bromoform for 3 or 4 days' use need be exposed to the air. Five grams of mercury per 100 ml. of bromoform were added as a stabilizer. When stored under laboratory conditions, out of direct sunlight, and tightly closed when not in use, no spectral changes resulted over a 2-month period, and the bromoform remained colorless. Decomposition products manifest through the development of additional infrared adsorption bands and yellow color, which slowly appear on prolonged exposure to air, can be removed by shaking with mercury. Purified bromoform can be heated for short periods on the steam bath if contact with air is minimized.

Methylene bromide (Dow Technical) was distilled at atmospheric pressure, and the forerun 10% was discarded. The main fraction, 80% (boiling point 97.5–98.5° C.), was stored in brown glass bottles, and the residue was discarded. The infrared spectrum of the distilled material was not significantly different from the starting material, and contained only very small bands not present in the spectrum published by Plyler (*18*). No efforts were expended in its further purification. This material was stable for at least 3 months, as judged by spectrometric criteria. Methylene bromide solutions can also be warmed for short periods on the steam bath without decomposition.

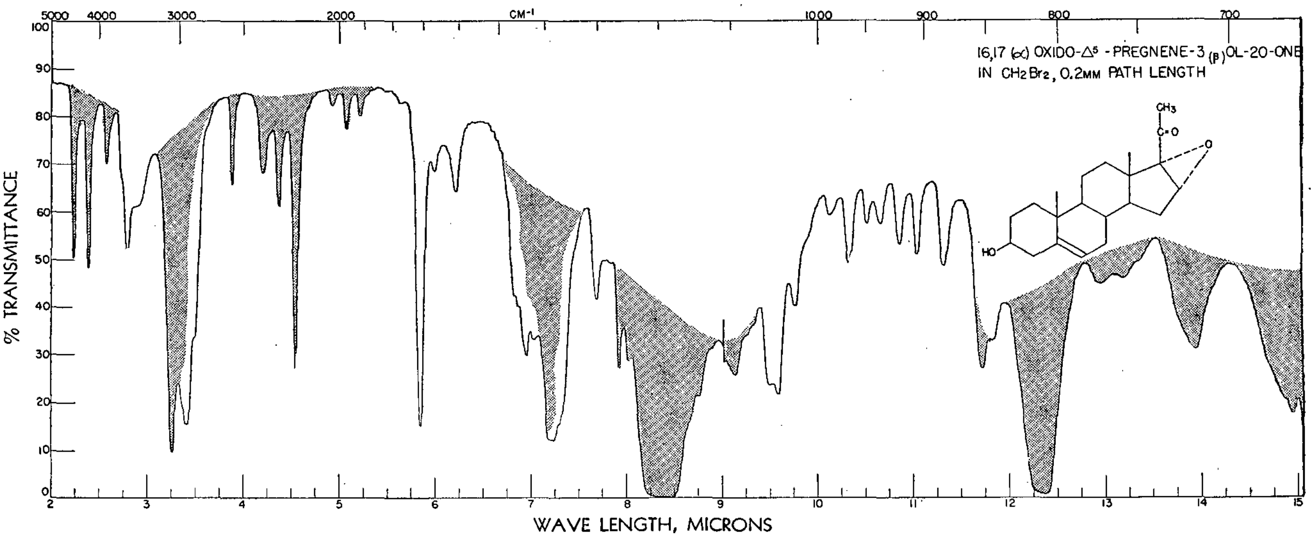

Figure 5. 16,17(α)-Oxido-Δ⁵-pregnene-3(β)ol-20-one in Methylene Bromide

25 mg. per ml.

Possible Reaction of Steroid Samples with Bromoform or Methylene Bromide. Over 125 spectra have been run in bromoform and methylene bromide, with no evidence of reaction between solute and solvent. Occasionally, solutions of steroids in bromoform have developed a noticeable yellow color after standing about 3 hours. The infrared spectra of such colored solutions even after standing for 3 days proved to be identical with those obtained immediately after dissolving. Furthermore, on shaking with mercury, the color was completely removed from the solutions with no resultant change in the infrared spectrum.

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Correlation of Infrared Spectra

Paraffins, Olefins, and Aromatics with Structural Groups

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This work was undertaken to improve the reliability and convenience of structural analyses of hydrocarbons by infrared spectra, and to provide factual data which might eventually aid in understanding the vibrational origins of certain bands. Correlations between the spectra and structural properties of paraffins, olefins, and aromatics are tabulated and charted in a manner convenient to the needs of the practicing spectroscopist. They should improve the reliability of structural analyses of hydrocarbons because (1) wave-length ranges for the correlation bands have been deduced from only hydrocarbon spectra. Often the ranges thus determined are considerably narrower than shown in data published heretofore. This makes the bands more definitive. (2) Intensity data are given. These are sometimes useful in identifying the structures giving rise to bands. In some cases they make possible estimates of the concentrations of groups. (3) Critical evaluations of the correlations are given. This makes the limitations involved in using any specific correlation band more evident.

A CORRELATION band is any band which empirical observation has demonstrated to be associated with a specific atom grouping (hereafter termed "structure"). Its presence in the spectrum of a material indicates that the structure may be present; its absence is certain evidence that the structure is missing.

Any correlation band will vary in position, depending on the environment of the associated structure. Most tables and charts of correlations assign wave-length ranges to the bands (*1, 3, 5, 10, 12*). Many correlations which have been deduced from the spectra of molecules involving nonhydrocarbon as well as hydrocarbon substituents are found to have much narrower ranges when they are deduced from hydrocarbon spectra only. Figure 8 illustrates this for the correlations for benzene ring substitutions. In making structural analyses of petroleum chemicals by infrared, it is useful to use correlation tables and charts giving the narrower wave-length ranges valid for the hydrocarbons.

This report presents correlation tables and charts for paraffinic, olefinic, and aromatic structures. The paraffin correlations were deduced from a study of paraffin spectra only; the olefins are from the spectra of unconjugated alkyl substituted compounds. The aromatic correlations were obtained partly from the spectra of alkyl aromatics and, where the data on hydrocarbons were limited, from a comparison of the spectra of alkyl aromatics with published correlation charts.

The problem of determining how the correlations given here for paraffinic structures are modified when these are adjacent to olefinic or aromatic structures, and of determining the effect on the olefinic and aromatic correlations when other hydrocarbon structures than alkyl groups are substituted, cannot be solved empirically without more data than are now available.

The spectral data on hydrocarbons are from the American Petroleum Institute catalog of infrared spectra of hydrocarbons. The aromatic correlations were partly deduced with the aid of charts issued by Sadtler (*12*) and the American Cyanamid Co. and Perkin Elmer Corp. (*1*, *5*). The spectra in the Sadtler catalog were also used for this purpose.

TABLES AND FIGURES

Tables. Tables I to VII are for paraffinic, Table VIII is for olefinic, and Tables IX and X are for aromatic correlations. For the paraffinic and aromatic correlations there are two types of tables. The first lists the structures which possess prominent correlation bands—i. e., intense and well defined as to position—and opposite each gives the bands, band intensities, and remarks about their properties. These tables are useful when the absence, or possible presence, of a particular sturcture is the information sought. The other type of table is the "inverse" and lists the wave lengths in decreasing order and opposite each wave length gives the correlated structure. This table is useful for identifying structures which may possibly be present in a material.

Table VI is unique. It lists, in decreasing order, the bands associated with the structural properties of long-chain paraffins and gives their intensities and remarks about their properties.

In all tables the most useful bands are underlined.

INTENSITIES. A knowledge of the intensities of correlation bands opens the way for measuring the concentrations of some structural types and reduces the chance of making erroneous structural deductions. For example, if a close proportionality is found between the maximum extinction of a correlation band and the concentration of the correlated structure, its concentration in an unknown sample can be measured (provided interfering absorptions are absent or can be corrected for). Furthermore, if such a proportionality exists, even roughly, for two or more correlation bands for a certain structure, their extinctions will have ratios which may be maintained in the spectrum of a sample containing the structure. If a sample exhibits bands at the correlating positions which do not have the proper intensity ratios, the bands must be there by accident and the presumed structure must be absent, or else the presumed structure is present but absorptions from other origins falling at one or more of its correlation wave lengths alter the intensity ratios. In any event, whenever absorption bands appear at all the correlation positions for a given structure and have the proper intensity ratios, the evidence in favor of the structure is greatly strengthened.

The intensities of the stronger correlation bands and of some weak bands are given in the tables in terms of maximum extinction per unit concentration of the absorbing structure (in moles per milliliter) per centimeter of absorbing path, unless otherwise stated. In addition to this intensity coefficient, the cell thickness used to bring out each correlation band in the spectra examined in this work is listed. This is a useful qualitative index of intensity, particularly for bands in the spectra of normal paraffins which arise from the CH_2 groups, or perhaps the carbon skeleton. Here the molar concentration of the absorbing structure is nearly constant over a wide range of molecular weights, and the extinction for any given cell is nearly the same for all normal paraffins. A similar constancy of extinction regardless of molecular weight is found for many of the weaker bands which project out from relatively much stronger absorptions in these and other spectra.

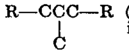
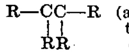
NOMENCLATURE AND SPECTRAL LIMITS.

Table I. Correlations for Sequences $CH_3—(CH_2)_n—$

Correlations have been obtained only for the dependence of position of the 12.7 to 13.9-micron band on the length of CH_2 sequences of the type $—(CH_2)_n—$ bounded at one or both ends by CH_3.

n	Band Position, (μ and Cm.$^{-1}$)	Intensity E/Mole/Ml./Cm. (per CH_2 Group)	Remarks
6 or more CH_2 sequences (16)	13.82–13.86 724–722	0.26 × 10^4 40–70% in 0.006-cm. cell	Intensity per CH_2 (0.25–0.26) × 10^4 except nC_{12} 0.22 × 10^4. 13.85–13.86 for 12 compounds, 13.82, 13.84 for two
5 (5)	13.82–13.84 724–723	0.28 × 10^4 0.006-cm. cell	Intensity between 0.27 and 0.29 × 10^4
4 (4)	13.78–13.81 726–724	0.29 × 10^4 0.006-cm. cell	Intensity between 0.27 and 0.31 × 10^4
3 (6)	13.71–13.77 729–726	0.35 × 10^4 0.006-cm. cell	Intensity between 0.33 and 0.38 × 10^4. 5-*n*-butyl-C_{16} has broad band which may be two bands. Evidence based on other than API spectra indicates that 4 CH_2's between certain branchings absorb here
2 (omit *n*-butane) (12)	13.46–13.62 743–734	0.5 × 10^4 0.006-cm cell	Intensity variable, partly because of overlapping absorptions. Some evidence indicates that 3 CH_2's between certain branchings absorb here and 2 CH_2 between certain branchings absorb between 13.0 and 13.4
1 (omit C_3H_8 3rd C must be a tertiary C) (17)	12.88–12.98 776–770	0.4 × 10^4 0.017-cm. cell	Intensity value very rough. Values range as high as 0.7 × 10^4
1 (3rd C must have two CH_3 groups) (8)	12.74–12.83 785–780	1 × 10^4 0.006-cm. cell	Intensity varies from as low as 0.4 × 10^4 to above 1 × 10^4. Other structures sometimes absorb in this region, and this obscures authenticity of assigning this band to indicated structure in some cases

Table II. Correlations for Methyl Groups Attached to Carbons with No Other Methyls

Structure	Band Position, μ and Cm.$^{-1}$	Intensity, E/Mole/Ml./Cm.	Remarks
Isolated CH_3	7.23–7.26 1383–1377	1.8 × 10^4 per CH_3. Generally in 0.001 cm. or smaller cell	Most useful band for isolated CH_3 group. Splits in characteristic manner when two or more methyls are attached to common carbon (see correlations for these structures). Intensity per CH_3 constant to roughly ±0.3 × 10^4 except in *n* paraffins below C_7, where it is smaller. This coefficient should be applicable to measurement of concentrations of isolated CH_3 groups
 $R—C\underset{\mid\atop C}{C}C—R$ (isolated internal methyl group) (13)	8.63–8.69 1159–1151	(0.5–0.9) × 10^4 per group 0.017 cm. cell	There is evidence that this band may be characteristic of isolated internal tertiary carbon atoms. However, it is most pronounced in spectra of compounds with isolated internal CH_3. This band is often obscured by stronger absorption at shorter wave length in spectra of compounds with 2 methyl and 2,2-dimethyl branchings
 $R—\underset{\mid\atop R}{C}\underset{\mid\atop R}{C}—R$ (adjacent tertiary carbon atoms) (10)	8.85–8.96 1130–1116	(1.1–3.1) × 10^4 per structure. 0.0056 cm. cell	Striking band in spectra of compounds with structure. However, some compounds with 2,2-dimethyl type of branching absorb here

In all the tables the letter R denotes any alkyl group.

A structural group is stated to be "isolated" from other structural groups when one or more CH_2 groups separate it from the others.

In tabulating intensity values the term "per group" is used. This signifies that the intensity coefficient listed is in terms of moles per milliliter of the particular structure listed.

The letter E denotes extinction.

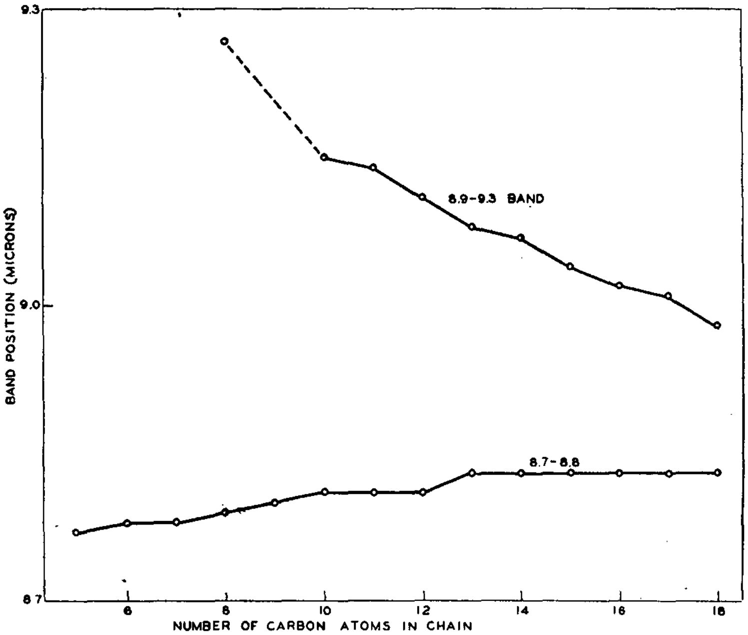


Figure 1. Band Position *vs.* Chain Length for Two Bands

In 8.9- to 9.5-micron region of infrared spectra of *n*-paraffins

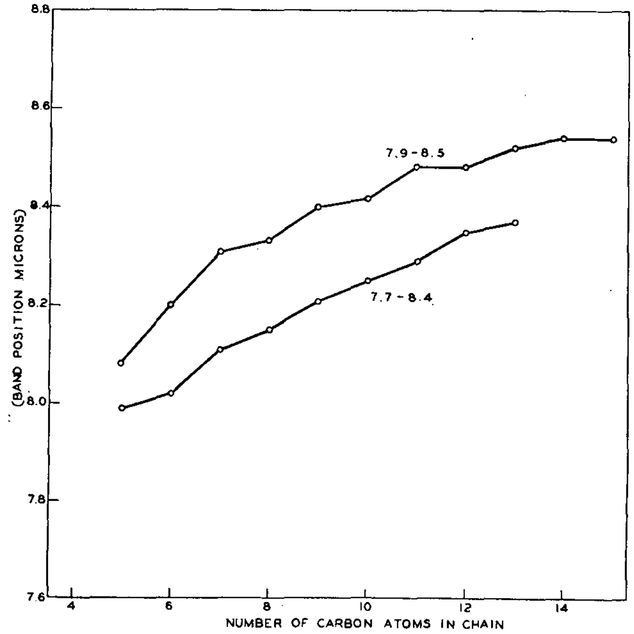


Figure 2. Band Position *vs.* Chain Length for Two Bands

In 7.5- to 8.5-micron region of infrared spectra of *n*-paraffins

The letter T is used for transmittance.

Except for parts of Tables IX and X, correlation bands are indicated as appearing between maximum and minimum wavelength limits which give the widest variations in the spectra of all available compounds. The method of setting the limits in the exceptional cases is described below. In some cases, these limits may not be wide enough.

Similarly, intensity variations, where given, are the maximum observed in available spectra and may not be wide enough for all cases.

NUMBER OF SPECTRA. The number of spectra compared in establishing each correlation in Tables I to VI, VIII, and IX are given below the respective structure.

Figures. Certain bands in the spectra of normal paraffins vary regularly in position with chain length. These dependences are shown graphically in Figures 1, 2, and 3.

Figures 4, 5, 6, and 7 show the positions of the correlation bands and their associated structures. The vertical heights of the charted areas index the band intensities in accordance with scales shown in the figures.

Figure 8 compares the ranges for aromatic structures deduced for all types of substitution (*5*) with those valid for alkyl substitution only.

CORRELATIONS FOR PARAFFINIC STRUCTURES

The correlations were determined by a systematic procedure in which structures were studied in such a sequence that, as far as possible, the study of a new structure involved only the spectra of molecules containing this structure and other structures that had been studied previously. At the start of this sequence were the normal paraffins. Correlations for branched structures were then sought, using first the spectra of compounds containing only straight-chain structures in addition to the structure under investigation. Then the spectra of compounds containing more than one type of branching structure separated from each other by at least one CH_2 group were investigated. Finally the spectra of compounds containing adjacent branched structures were examined. This systematic approach minimized the chance of con-

(*Continued on page 322*)

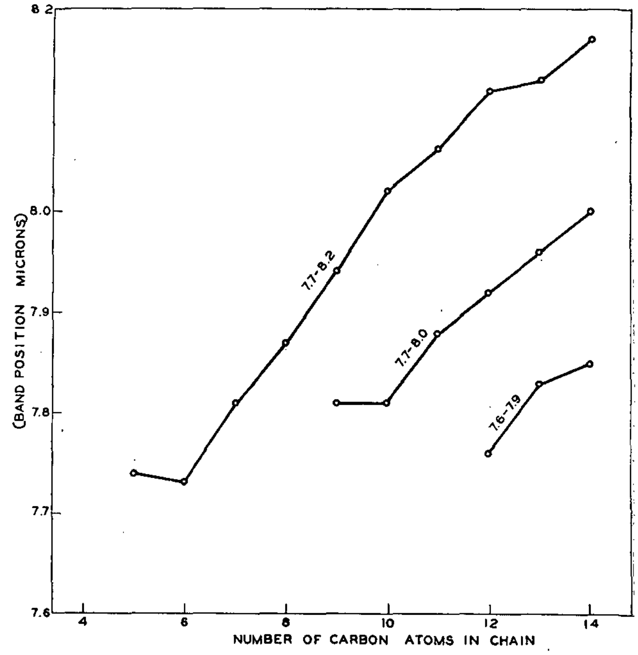


Figure 3. Band Position *vs.* Chain Length for Three Bands

In 7.6- to 8.2-micron region of infrared spectra of *n*-paraffins

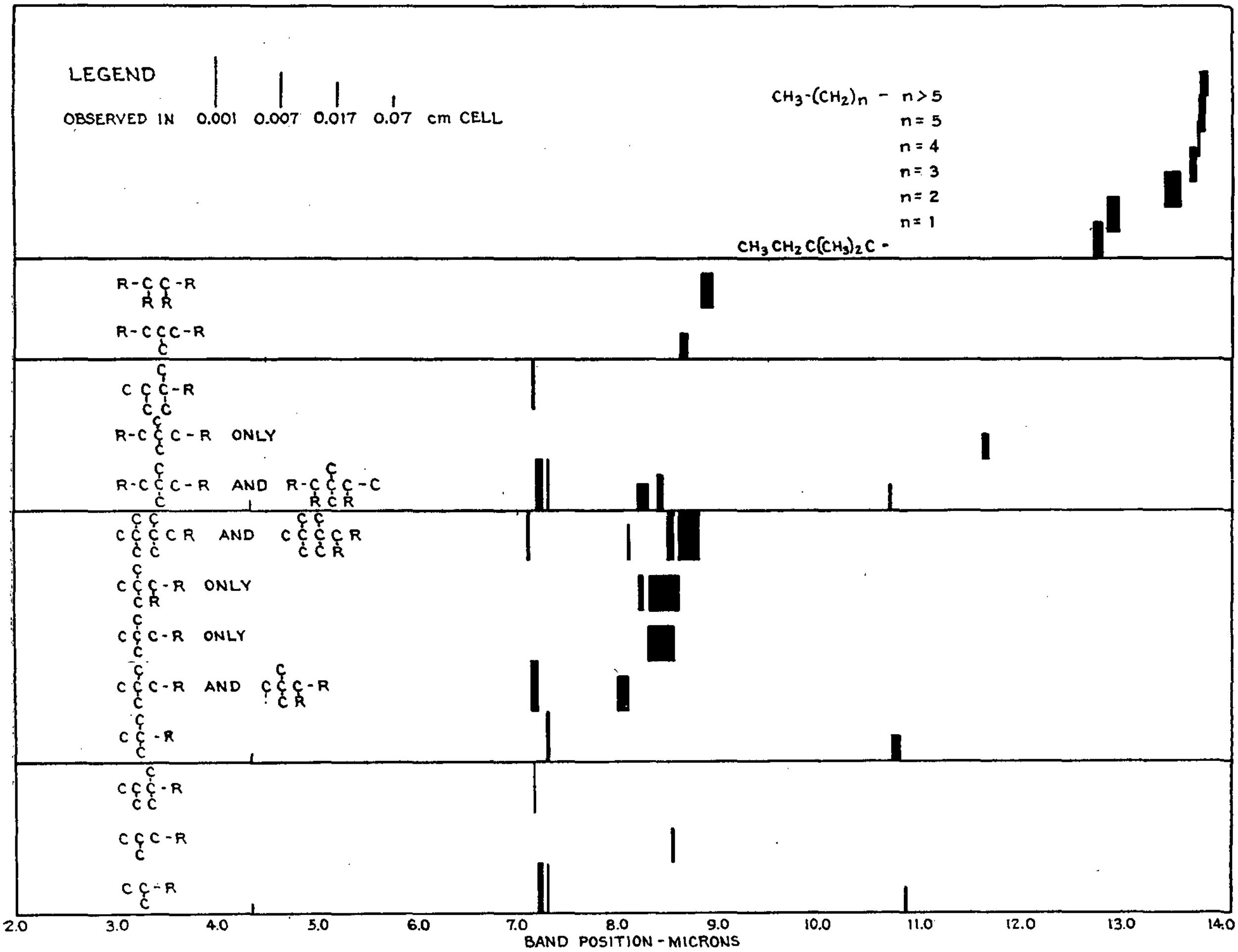


Figure 4. Correlation Bands for Paraffinic Structures

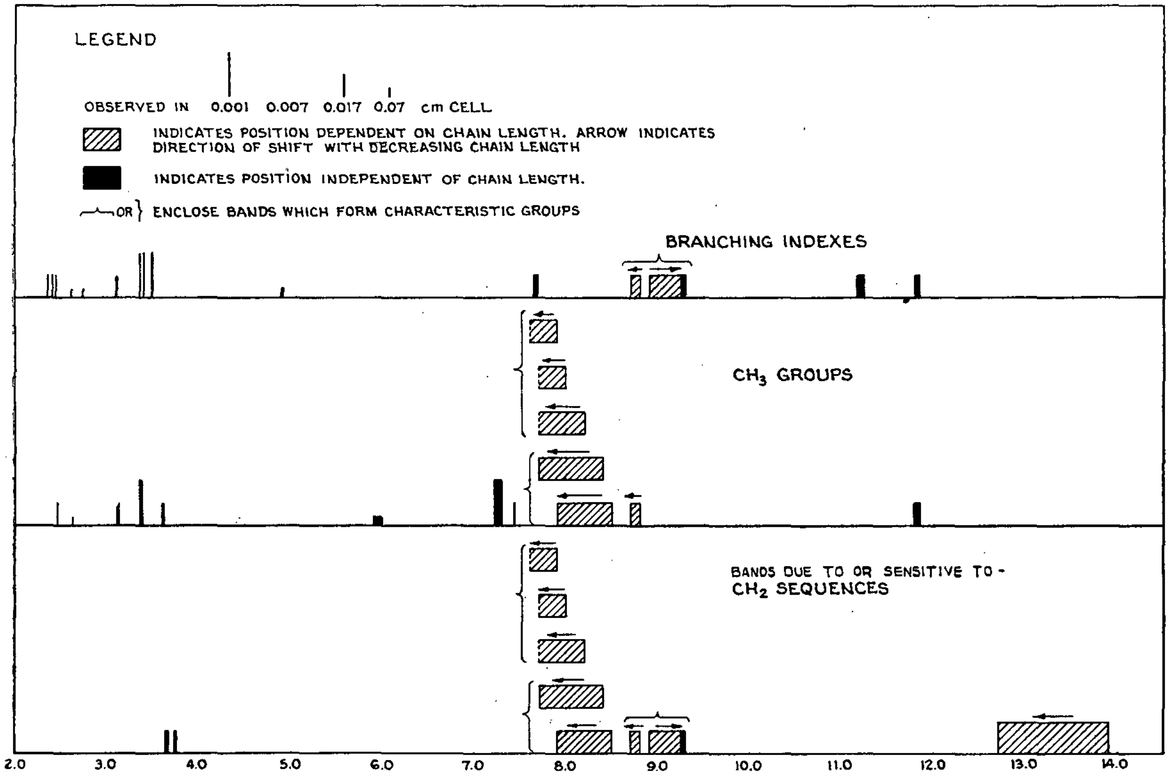
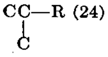
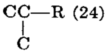
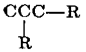
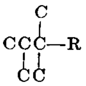


Figure 5. Spectral Features of Long-Chain Paraffins

Table III. Correlations for Two Methyl Groups on a Common Tertiary Carbon

(2-methyl type branching)

Absorptions from isolated $—\overset{\substack{C\\|}}{\underset{\substack{|\\C}}{C}}—$ interfere with all bands for this group but one (8.55μ), absorptions from isolated $C\overset{\substack{C\\|}}{\underset{\substack{|\\C}}{C}}—$ structures interfere with all but two (8.55 and 7.20μ). When $—\overset{\substack{C\\|}}{\underset{\substack{|\\C}}{C}}—$ or $C\overset{\substack{C\\|}}{\underset{\substack{|\\C}}{C}}—$ are adjacent to tertiary or quaternary carbon atoms they may cause bands which fall at all positions of correlation bands for $C\underset{\substack{|\\C}}{C}—$. Fortunately, presence of these interfering groups may possibly be detected, as they possess correlation bands not interfered with by those for $C\underset{\substack{|\\C}}{C}—$.

Structure	Band Position, μ and Cm.⁻¹	Intensity, E/Mole/Ml./Cm.	Remarks
 $C\underset{\substack{\vert\\C}}{C}—R$ (24)	10.85–10.88 922–919	0.5 × 10⁴ (per $C\underset{\substack{\vert\\C}}{C}—$) 0.017 cm. cell	Clearly defined, sharp except when R contains $C\overset{\substack{C\\\vert}}{\underset{\substack{\vert\\C}}{C}}—$ or $—\overset{\substack{C\\\vert}}{\underset{\substack{\vert\\C}}{C}}—$ or in some spectra where branching is adjacent to $C\underset{\substack{\vert\\C}}{C}—$. Intensity widely variable between 0.3 and 0.8 × 10⁴ but generally around 0.5 × 10⁴
	7.29–7.31 1372–1368	4 × 10⁴ (per $C\underset{\substack{\vert\\C}}{C}—$) 0.001 cm. cell	Displacement from 7.25 position characteristic of isolated CH_3. However, $C\overset{\substack{C\\\vert}}{\underset{\substack{\vert\\C}}{C}}—$ and $—\overset{\substack{C\\\vert}}{\underset{\substack{\vert\\C}}{C}}—$ also absorb here. Intensity per group varies between 3 and 5 × 10⁴
	7.20–7.24 1389–1381	4 × 10⁴ (per $C\underset{\substack{\vert\\C}}{C}—$) 0.01 cm. cell	$—\overset{\substack{C\\\vert}}{\underset{\substack{\vert\\C}}{C}}—$ also absorbs here, but absorption from $C\overset{\substack{C\\\vert}}{\underset{\substack{\vert\\C}}{C}}—$ is at shorter wave lengths. Intensities vary from 3 to about 7 × 10⁴ but are near 4 generally
 $C\underset{\substack{\vert\\C}}{C}—R$ (24)	4.37–4.39 2290–2280	0.01 × 10⁴ (per carbon atom) 0.073 cm. cell	$C\overset{\substack{C\\\vert}}{\underset{\substack{\vert\\C}}{C}}—$ and $—\overset{\substack{C\\\vert}}{\underset{\substack{\vert\\C}}{C}}—$ absorb at lower end, and just below lower end, of this region. Intensity per carbon constant to about 10 to 15%. In $C\underset{\substack{\vert\\C}}{C}\underset{\substack{\vert\\R}}{C}—R$ this band is much less pronounced than in $C\underset{\substack{\vert\\C}}{C}C—R$. Band is not so prominent as its counterpart due to $C\overset{\substack{C\\\vert}}{\underset{\substack{\vert\\C}}{C}}—$
 $C\underset{\substack{\vert\\R}}{C}C—R$ (18)	8.54–8.56 1171–1168	1 × 10⁴ (per $C\underset{\substack{\vert\\C}}{C}—$) 0.006 cm. cell	Sometimes accompanied by another of comparable intensity at 8.69–8.77. Most compounds have intensities per group of between 0.9 and 1.2 × 10⁴. When branching occurs at third carbon this band is apparently displaced toward longer wave lengths, but more data are needed to associate displacement with type of branching
 $C\underset{\substack{\vert\\C}}{C}\overset{\substack{C\\\vert}}{\underset{\substack{\vert\\C}}{C}}—R$ (3)	7.16–7.17 1397–1395	3 × 10⁴ per group. 0.001 cm. cell or thinner	Only three examples, but it is striking that in these, and only in these, do bands appear at wave lengths shorter than 7.19–7.23, the region in which these groups absorb when separated from each other

fusing bands due to one structure with those of another and helped in determining the effect of environment on the correlation bands for each structure.

Tables I to V list the structures and their associated correlation bands, the sequence being from the unbranched to progressively more branched structures. Table VII is the inverse of these.

In Tables I to V the bands for a specific structure which arise regardless of the structure's environment are given first, then those restricted to specific environments. To illustrate: For the structure consisting of three methyls on a common carbon (2,2-dimethyl branching; see Table IV) there are several correlation bands which appear regardless of whether the carbon adjacent to the structure is secondary, tertiary, or quaternary. These correlations are listed first. Another band specific to the case where the adjacent carbons are tertiary is tabulated next, followed by several which correlate when a carbon with two methyl groups is adjacent.

Table VI lists, in order of decreasing wave length, bands related to the structures of long-chain paraffins, together with information about their intensities and properties. They are less prominent spectral features than the bands in Tables I to V. The inverse to Table VI is not included.

CORRELATIONS OF OLEFINS

The appearance of one double bond in an otherwise paraffinic molecule produces characteristic absorption bands in the rock salt region which are for the most part intense as compared with the correlation bands for paraffins. Only one table giving the structures and opposite these their correlation bands, is presented, as the correlations discussed are limited to five types of structures. Figure 6 should prove helpful in obtaining a qualitative analysis from an inspection of the infrared spectrum of a sample. Some extrapolations of these correlations to polymers have been reported as giving useful information (*8*, *9*).

Because the number of olefin spectra is limited, the wave-length ranges given may not always be wide enough.

CORRELATIONS FOR ALKYLBENZENES

The correlations for the monoalkylbenzene substitution were obtained in the usual manner by comparing the available spectra of the monoalkylbenzenes. The ranges are much narrower than those given in Colthup's chart (*5*) for monosubstitution. How-

(*Continued on page 332*)

Table IV. Correlations for Three Methyl Groups on a Common Carbon

(2,2-Dimethyl type branching)

One group of bands is common to all molecules containing this structure regardless of the branching adjacent to the structure. These are given first. Then those common to the isolated group and the $\mathrm{\underset{C}{C}\overset{C}{\underset{R}{C}}C-R}$ structure, then those characteristic of isolated $\mathrm{C\overset{C}{\underset{C}{C}}-}$ alone, characteristic of $\mathrm{\underset{C}{C}\overset{C}{\underset{R}{C}}C-R}$ alone, and $\mathrm{\overset{C}{\underset{C}{C}}\overset{C}{\underset{C}{C}}C-R}$ alone. The band near 8.0 μ is most specific for identification of this structure. It varies slightly with environment, but there are few, if any, conflicting absorptions. Several correlation bands for this structure fall near those for $\mathrm{\underset{C}{C}C-}$ and $\mathrm{-\overset{C}{\underset{C}{C}}-}$. Therefore, if the $\mathrm{C\overset{C}{\underset{C}{C}}-}$ structure is present it may be difficult to detect these others, or to prove their absences

Structure	Band Position, μ and Cm.⁻¹	Intensity, E/Mole/Ml./Cm.	Remarks
$\mathrm{C\overset{C}{\underset{C}{C}}-R}$ ($\mathrm{C\overset{C}{\underset{C}{C}}-}$ regardless of branching adjacent to $\mathrm{C\overset{C}{\underset{C}{C}}-}$) (20)	10.73–10.80 932–926	0.4×10^4	$\mathrm{\underset{C}{C}\overset{C}{\underset{\underset{C}{C}}{C}}CCC}$ is an exception, either has no band or is absorbed in one at 10.97. Most intensity data of uncertain value because of absorption from adjacent bands. Intensity varies between 0.2 and 0.7×10^4
	7.28–7.32 1374–1366	8×10^4 (per $\mathrm{C\overset{C}{\underset{C}{C}}-}$) 0.001 cm. cell	$-\overset{\vert}{\underset{C}{\mathrm{C}}}-$, and $\mathrm{\underset{C}{C}C-}$ also absorb here, but in $\mathrm{C\overset{C}{\underset{C}{C}}-}$ this band is stronger relative to its short wave length partner than for others. Intensity variable partly because of overlapping absorptions. Variation $(6.4–11) \times 10^4$
	4.35–4.37 2300–2290	0.10×10^4 (per carbon atom) 0.073 cm. cell	$\mathrm{C\overset{C}{\underset{C}{C}}-}$ spectra in this region are distinguished by prominence with which this band and one near 4.15 stand out, much more so than for other spectra generally. Intensity per carbon atom constant to within about 10% for most spectra
$\mathrm{C\overset{C}{\underset{C}{C}}C-R}$ and $\mathrm{\underset{C}{C}\overset{C}{\underset{R}{C}}C-R}$	7.98–8.10 1253–1235	2×10^4 (per $\mathrm{C\overset{C}{\underset{C}{C}}-}$) 0.006 cm. cell	$\mathrm{C\overset{C}{\underset{C}{C}}-}$ always absorbs near 8.0 μ, exact position depending on environment. Intensity varies between 0.4×10^4 and 4×10^4
$\mathrm{C\overset{C}{\underset{C}{C}}C-R}$ and $\mathrm{\underset{C}{C}\overset{C}{\underset{R}{C}}C-R}$ *(Contd.)*	7.14–7.18 1401–1393	4×10^4 (per $\mathrm{C\overset{C}{\underset{C}{C}}-}$) 0.001 cm. cell	Characteristic of $\mathrm{C\overset{C}{\underset{C}{C}}-}$ structure is that 7.30 band is markedly stronger than this one at shorter wave lengths. Intensity variation from 2 to 5×10^4
$\mathrm{C\overset{C}{\underset{C}{C}}C-R}$ only (10)	8.28–8.54 1208–1171	1.6×10^4 (per $\mathrm{C\overset{C}{\underset{C}{C}}-}$) 0.006 cm. cell	Similar to 8.31–8.60 for $\mathrm{\underset{C}{C}\overset{C}{\underset{R}{C}}C-R}$ but better defined as to position Overlaps important regions for $\mathrm{\underset{C}{C}C-R}$ and $\mathrm{-\overset{C}{\underset{C}{C}}-}$. Most of these molecules absorb between 8.27 and 8.31. Intensities between 1.2×10^4 and 2.1×10^4
$\mathrm{\underset{C}{C}\overset{C}{\underset{R}{C}}C-R}$ only (5)	8.31–8.60 1203–1163	1.5×10^4 0.006 cm. cell	Apparently same band with wider limits as 8.28–8.54 for isolated $\mathrm{C\overset{C}{\underset{C}{C}}-}$. Intensity constant. Variation 1.2 to 1.7×10^4. Overlaps region important for $\mathrm{C\underset{C}{C}C-R}$ and $\mathrm{-\overset{C}{\underset{C}{C}}-}$
	8.21–8.24 1218–1214	2×10^4 0.006 cm. cell	Not in spectra of isolated $\mathrm{C\overset{C}{\underset{C}{C}}-}$. Overlapping from adjacent bands makes intensity data variable between 1.0 and 2.6×10^4. $\mathrm{-\overset{C}{\underset{C}{C}}-}$ structures also absorb in this region

(*Continued on next page*)

Table IV. (*Continued*)

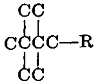
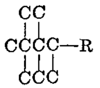
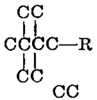
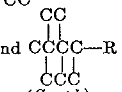
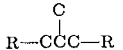
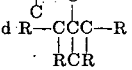
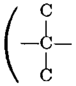
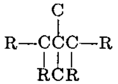
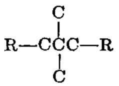
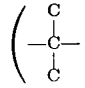
Structure	Band Position μ and Cm.$^{-}$	Intensity, E/Mmole/Ml./Cm.	Remarks
 $\mathrm{C\underset{C}{\overset{C}{C}}\underset{C}{\overset{C}{C}}C{-}R}$	8.6–8.8 1160–1140	6 × 10^4 0.001 cm. cell	See also bands for $\mathrm{C\underset{C}{\overset{C}{C}}{-}R}$
and  $\mathrm{C\underset{C}{\overset{C}{C}}\underset{C}{\overset{C}{C}}\underset{C}{C}{-}R}$	8.5–8.6 1180–1160	4 × 10^4 0.001 cm. cell	These two strong bands are outstanding features of spectra of three molecules available with this structure. When observed in spectrum with another strong band at slightly longer wave lengths than usual $\mathrm{C\underset{C}{\overset{C}{C}}{-}}$ absorption at 8 microns this structure is suggested. However, small number of compounds for structure is a weak point. Intensities of the 8.6 band are (5.4, 5.8, 8.2) × 10^4
 $\mathrm{C\underset{C}{\overset{C}{C}}\underset{C}{\overset{C}{C}}C{-}R}$	8.10–8.12 1235–1232	1 × 10^4 0.006 cm. cell	Just a bit longer in wave length than 8.0 band for other $\mathrm{C\underset{C}{\overset{C}{C}}{-}}$ structures. Intensities (0.97, 0.70, 1.0) × 10^4
and  $\mathrm{C\underset{C}{\overset{C}{C}}\underset{C}{\overset{C}{C}}\underset{C}{C}{-}R}$ (*Contd.*)	7.10–7.12 1408–1404	3 × 10^4 0.001 cm. cell	A bit shorter in wave length than 7.14–7.18 band for other $\mathrm{C\underset{C}{\overset{C}{C}}{-}}$. Intensities (3.5, 2.9, 2.9) × 10$_4$

Table V. Correlations for Dimethyl Branching from a Common Carbon Not Adjacent to an End Carbon

The correlations for this group depend on its environment, there being no bands which characterize this structure regardless of its environment. Correlations given are for $\mathrm{R{-}\underset{R}{C}\underset{C}{\overset{C}{C}}\underset{R}{C}{-}R}$ and $\mathrm{R{-}C\underset{C}{\overset{C}{C}}C{-}R}$, $\mathrm{R{-}C\underset{C}{\overset{C}{C}}C{-}R}$ only, and $\mathrm{C\underset{C}{C}\underset{C}{\overset{C}{C}}{-}R}$. Correlations for $\mathrm{C\underset{C}{\overset{C}{C}}\underset{C}{\overset{C}{C}}\underset{R}{C}{-}R}$ appear in Table IV. Bands originating from $\mathrm{C\underset{C}{\overset{C}{C}}{-}}$ and $\mathrm{C\underset{C}{C}{-}}$ structures interfere with all but one correlation for the $\mathrm{{-}\underset{C}{\overset{C}{C}}{-}}$ structures (that at 11.65 to 11.69μ for the $\mathrm{R{-}C\underset{C}{\overset{C}{C}}C{-}R}$ structure). Particularly when $\mathrm{C\underset{C}{\overset{C}{C}}{-}}$ structures are present, it may be difficult to say much about the presence or absence of $\mathrm{{-}\underset{C}{\overset{C}{C}}{-}}$ structures. Too few data are available to indicate the effects of structures like $\mathrm{R{-}C\underset{C}{\overset{C}{C}}\underset{C}{\overset{C}{C}}C{-}R}$.

Structure	Band Position, μ and Cm.$^{-1}$	Intensity, E/Mole/Ml./Cm.	Remarks
 $\mathrm{R{-}C\underset{C}{\overset{C}{C}}C{-}R}$ and  $\mathrm{R{-}\underset{R}{C}\underset{C}{\overset{C}{C}}\underset{R}{C}{-}R}$	10.71–10.73 934–932	(0.2–0.6) × 10^4 per group. 25–65% T in 0.017 cm. cell	Intensity apparently increases when tertiary carbon is adjacent to structure. This band is just at shorter wave lengths than a similar one for 2,2-dimethyl branching and is obscured by latter band when 2,2-dimethyl structure is present (see Table IV)
 ($\mathrm{{-}\underset{C}{\overset{C}{C}}{-}}$ with or without adjacent tertiary carbons) (9)	8.39–8.44 1192–1185	1.0 × 10^4 per group. 35–55% T in 0.0056 cm. cell	Intensity per group (0.8–1.2) × 10^4. 2,2-dimethyl adjacent to tertiary carbon interferes
	8.19–8.29 1221–1206	(0.2–0.8) × 10^4 per group. 20–30% T in 0.017 cm. cell	For all but one intensity (0.5–0.8) × 10^4. When group is isolated, limits are 8.21–8.25. Interfered with by band from 2,2-dimethyl structures adjacent to tertiary carbon
 $\mathrm{R{-}\underset{R}{C}\underset{C}{\overset{C}{C}}\underset{R}{C}{-}R}$  $\mathrm{R{-}C\underset{C}{\overset{C}{C}}C{-}R}$	7.31–7.32 1368–1366	5 × 10^4 per group. 0.001 cm. or thinner cell	Intensity (3.9–7.3) × 10^4. Same position as for 2-methyl and 2,2-dimethyl branchings
 ($\mathrm{{-}\underset{C}{\overset{C}{C}}{-}}$ with or without adjacent tertiary carbons) continued (9)	7.19–7.24 1391–1381	4 × 10^4 per group. 0.001 cm. or thinner cell	Evident only as shoulder on side of 7.25 isolated CH_3 group band in spectra of those compounds where equal or greater number of isolated CH_3 groups are present and other structures absorbing in 7.19–7.24 range are absent
	4.35 2300	40–50% T in 0.07 cm. cell	Generally prominent sharp projection from relatively stronger background. Intensity per carbon close to 0.01 × 10^4

(*Continued on next page*)

Table V. (*Continued*)

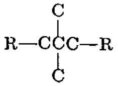
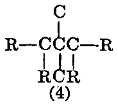
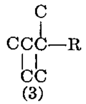
Structure	Band Position, μ and Cm.$^{-1}$	Intensity, E/Mole/Ml./Cm.	Remarks
 but not  (4)	11.65–11.69 868–855	0.2 × 10^4 per group. 0.017 cm. cell	Only 4 examples, but distinctive appearance of this band in their spectra is suggestive of a correlation. Intensity (0.14–0.27) × 10^4
 (3)	7.16–7.17 1397–1395	3 × 10^4 per group. 0.001 cm. cell or thinner	Only 3 examples, but it is striking that in these, and only these, cases are there bands below 7.19–7.23, the region in which these groups absorb when separate

Table VI. Characteristics of Long-Chain Paraffin Spectra

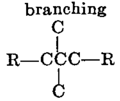
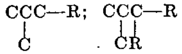
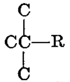
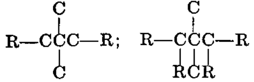
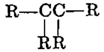
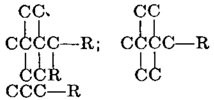
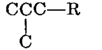
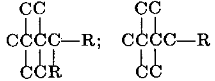
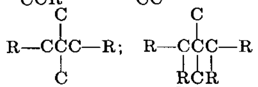
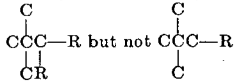
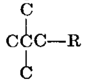
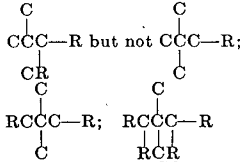
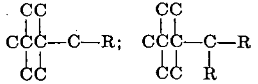
Structural Feature	Band Position, μ and Cm.$^{-1}$	Intensity, E/Mole/Ml./Cm.	Remarks
CH_3 groups	11.78–11.85 849–844	0.1 × 10^4 per CH_3 60–70% T in 0.017 cm. cell	Weak band. Found in nC_8 and higher, becoming weaker with increasing chain length. Association with CH_3 uncertain on account of large relative background absorption
CH_2 sequences	9.25–9.31 1081–1074 8.9–9.3 1120–1080 8.7–8.8 1150–1140	0.034 × 10^4 per CH_2 50–60% T in 0.017 cm. cell (0.3–0.4) × 10^4 per molecule. 40–65% T in 0.017 cm. cell 0.2 × 10^4 per CH_3 35–65% T in 0.017 cm. cell	Characteristic triplet in spectra of *n* paraffins above nC_{10}. Band position varies with chain length for *n*-paraffins (see Figure 1), 8.7–8.8 band increases in intensity with decreased chain length. 8.9–9.3 band merges with 9.25–9.31 band in lower *n*-paraffin spectra
CH_2 sequences	7.9–8.5 1270–1180 7.7–8.4 1300–1190	0.1 × 10^4 per CH_3 55–65% T in 0.017 cm. cell 0.1 × 10^4 per CH_3 50–65% T in 0.017 cm. cell.	Characteristic pair in spectra of medium length chains. Move toward shorter wave length as chain length decreases (Figure 2). 7.9–8.5 band barely detectable in spectra above nC_{14}. 7.7–8.4 band not detectable above nC_{13}, and less easily identifiable than 7.9–8.5 in spectra of lower *n*-paraffins. Neither band easily identifiable in spectra of highly branched paraffins. Intensities increase with reduction in chain length in *n*-paraffin spectra, suggesting bands may be associated with CH_3 groups
CH_2 sequences	<7.7–8.2 >1300–1220 <7.7–8.0 >1300–1250 <7.6–7.9 >1320–1270	0.16 × 10^4 per CH_3 40–60% T in 0.017 cm. cell 0.2 × 10^4 per CH_3 35–55% T in 0.017 cm. cell 0.4 × 10^4 per CH_3 approx. 40% T in 0.017 cm. cell	Characteristic group of three in spectra of chains of intermediate length. Not clearly evident in *n*-paraffin spectra above nC_{14}. All three bands move progressively toward shorter wave length as chain length decreases (Figure 3). 7.6–7.9 band merges with other absorptions in spectra of shorter chain compounds. Branching often introduces other bands into this region or causes modifications which make identification hard. Spectra of *n*-paraffins above nC_{14} have band of moderate intensity near 7.65 and nothing between this and 8.2 (< indicates lower limit is less than figure given)
Branching index	7.65–7.70 1307–1299	0.08 × 10^4 per CH_2 20–40% T in 0.017 cm. cell	Particularly striking in spectra of *n*-paraffins above nC_9. Identity obscure in spectra of many highly branched compounds. Branching often introduces more bands in this vicinity and appears also to enhance intensity
CH_3 groups	7.44 1344	15–25% T in 0.017 cm. cell	Projects from much stronger background but increases markedly in spectra of lower *n*-paraffins relative to higher. Band enhanced in spectra of many compounds with isolated 2-methyl branching but position and intensity follow no regular pattern in branched chain spectra
CH_3, CH_2, possibly CH groups	6.75–7.0 1481–1430	Observed in 0.001 cm. cell or thinner	Some evidence that 2,2-dimethyl branching causes absorption at short wave-length end of this region
Branching index	4.88–4.92 2050–2030	40–55% T in 0.07 cm. cell	Projects from relatively stronger background. Significant thing is that it is clearly defined in spectra of compounds with long-chain structures and in all *n*-paraffin spectra, but it is difficult to identify and may be accompanied by other bands when branching (at least methyl branching) is present. Presence of such complicating features implies branching
CH_2 sequences, branching	3.73–3.75 2680–2670 3.65–3.67 2740–2720	0.07 × 10^4 per CH_2 30–50% T in 0.017 cm. cell 0.06 × 10^4 per carbon atom. 50–65% T in 0.017 cm. cell	If these are only bands in 3.5–4.0 region and if 3.73 is stronger than 3.65, long chains are indicated. 3.73 intensity exceeds 3.65 in nC_{18} spectrum, is about equal nC_{17} through nC_{15}, thereafter has lower extinction. 3.65 band is further enhanced relative to 3.73 in spectra of branched compounds. However, many branched paraffins have more than these two bands in this region of their spectra. 3.65 band projects from strong background absorption. Its extinction is not proportional to number of CH_3 groups
Branching index	3.47–3.49 2880–2870 3.39–3.42 2950–2920 3.35–3.38 2990–2960	1.3 × 10^4 per carbon. Observed in 0.001 cm. or thinner cell 2 × 10^4 per CH_2. 0.001 cm. or thinner cell 7 × 10^4 per CH_3. 0.001 cm. or thinner cell	3.47 band evident in all *n* paraffin spectra but less prominent than 3.39 and 3.35 in many spectra of branched paraffins, absent in some such spectra. Relative intensity of 3.35 and 3.39 seems to index relative number of CH_3 to CH_2 groups in that when 3.35 is equal to 3.39 this ratio seems to be about 0.8 and for greater CH_3 contribution 3.35 becomes greater and may completely obscure 3.39 in spectra of very highly branched structures with few CH_2 groups. Good resolution needed to bring out these details

(*Continued on next page*)

Table VI. (*Continued*)

Structural Feature	Band Position, μ and Cm.$^{-1}$	Intensity, E/Mole/Ml./Cm.	Remarks
CH$_3$ groups, branching	3.10–3.13 3230–3190	0.08 × 10^4 per CH$_3$ 40–60% T in 0.017 cm. cell	Origin not certain but relatively stronger in spectra of lower n-paraffins and branched paraffins which suggests CH$_3$ groups as responsible. Not detectable in spectra of paraffins above nC$_{10}$
Branching index	2.5–2.8 region 4000–6000	Observed in 0.07 cm. cell	n-paraffin spectra above nC$_6$ exhibit only 2.75 band as pronounced projection from the strong background. In spectra of branched compounds where number of CH$_3$ groups is relatively high 2.62 band becomes enhanced and 2.75 may be hardly noticeable. Many branched compounds have more than two bands in this region
	2.75 3640	0.009 × 10^4 per carbon. 40–60% in 0.07 cm. cell	
	2.62 3820	45–55% T in 0.07 cm. cell	
CH$_3$ groups, branching	2.45–2.46 4080–4070	50–60% T in 0.017-cm. cell	2.45 band is barely evident as shoulder in spectra of n-paraffins above nC$_9$. In lower paraffin spectra and in spectra of compounds with branching it increases relative to 2.40 band as relative number of CH$_3$ groups increases. 2.40 band is difficult to detect in spectra of some branched-chain compounds. 2.35 band is present in all n-paraffin spectra and some spectra of branched-chain compounds. It is significantly absent in spectra of compounds containing 2,2-dimethyl and internal dimethyl as only branchings
	2.40–2.42 4170–4130	50–60% T in 0.017 cm. cell	
	2.35–2.37 4260–4220	40–45% T in 0.017-cm. cell	
	2.31–2.33 4330–4290	0.04 × 10^4 per carbon 45–55% T in 0.017 cm. cell	2.31 band stands out in all paraffin spectra studied. Good resolution is needed to bring out these details

Table VII. Correlation Bands in the 2- to 15-Micron Region and Their Associated Structures

Band Position, μ and Cm.$^{-1}$	Structure	Intensity, E/Mole/Ml./Cm.	Table
13.82–13.86 724–722	6 or more CH$_2$ with CH$_3$ on at least one end	0.26 × 10^4 per CH$_2$ 0.006 cm. cell	I
13.82–13.84 724–723	5 CH$_2$ with CH$_3$ on at least one end	0.28 × 10^4 per CH$_2$ 0.006 cm. cell	I
13.78–13.81 726–724	4 CH$_2$ with CH$_3$ on at least one end	0.29 × 10^4 per CH$_2$ 0.006 cm. cell	I
13.71–13.77 729–726	3 CH$_2$ with CH$_3$ on at least one end	0.35 × 10^4 per CH$_2$ 0.006 cm. cell	I
13.46–13.62 743–734	2 CH$_2$ with CH$_3$ on one end. Omit n-butane	0.5 × 10^4 per CH$_2$ 0.006 cm. cell	I
12.88–12.98 776–770	1 CH$_2$ between CH$_3$ and tertiary carbon	0.4 × 10^4 per CH$_2$ 0.006 cm. cell	I
12.74–12.83 785–780	CH$_2$ sequence, 1 CH$_2$ between CH$_3$ and dimethyl branching	1 × 10^4 per CH$_2$ 0.006 cm. cell	I
11.65–11.69 858–855	 $R—C\overset{C}{\underset{C}{C}}C—R$	0.2 × 10^4 per group 0.017 cm. cell	V
10.85–10.88 922–919	 $\underset{C}{C}CC—R;\ \underset{C}{C}\underset{R}{C}C—R$	0.5 × 10^4 per group 0.017 cm. cell	III
10.73–10.80 932–926	 $C\overset{C}{\underset{C}{C}}—R$	0.4 × 10^4	IV
10.71–10.73 934–932	 $R—C\overset{C}{\underset{C}{C}}C—R;\ R—\underset{R}{C}\overset{C}{\underset{C}{C}}\underset{R}{C}—R$	(0.2–0.6) × 10^4 per group. Generally in 0.017 cm. cell	V
8.85–8.96 1130–1116	 $R—\underset{R}{C}\underset{R}{C}—R$ (adjacent tertiary carbons)	(1.1–3.1) × 10^4 0.006 cm. cell	II
8.63–8.69 1159–1151	 $R—C\underset{C}{C}C—R$	(0.5–0.9) × 10^4 per group in 0.017 cm. cell	II
8.6–8.8 1160–1140	 $C\overset{C}{\underset{C}{C}}\overset{C}{\underset{C}{C}}\underset{R}{C}—R;\ C\overset{C}{\underset{C}{C}}\overset{C}{\underset{C}{C}}C—R$	6 × 10^4 per group 0.001 cm. cell.	IV
8.54–8.56 1171–1168	 $\underset{C}{C}CC—R$	1 × 10^4 per group. 0.006 cm. cell	III
8.5–8.6 1180–1160	 $C\overset{C}{\underset{C}{C}}\overset{C}{\underset{C}{C}}\underset{R}{C}—R;\ C\overset{C}{\underset{C}{C}}\overset{C}{\underset{C}{C}}C—R$	4 × 10^4 per group. 0.001 cm. cell	IV
8.39–8.44 1192–1185	 $R—C\overset{C}{\underset{C}{C}}C—R;\ R—\underset{R}{C}\overset{C}{\underset{C}{C}}\underset{R}{C}—R$	1.0 × 10^4 per group. 35–55% T in 0.006 cm. cell	V
8.31–8.60 1203–1163	 $C\overset{C}{\underset{C}{C}}\underset{R}{C}—R$ but not $C\overset{C}{\underset{C}{C}}C—R$	1.5 × 10^4 per group. In 0.006 cm. cell	IV
8.28–8.54 1208–1171	 $C\overset{C}{\underset{C}{C}}C—R$	1.6 × 10^4 per group. In 0.006 cm. cell	IV
8.19–8.29 1221–1206	 $C\overset{C}{C}\underset{R}{C}—R$ but not $C\overset{C}{\underset{C}{C}}C—R;$ $RC\overset{C}{\underset{C}{C}}C—R;\ R\underset{R}{C}\overset{C}{\underset{C}{C}}\underset{R}{C}—R$	Generally in 0.006 or 0.017 cm. cells. See notes to tables	IV V
8.10–8.12	 $C\overset{C}{\underset{C}{C}}\overset{C}{\underset{C}{C}}—C—R;\ C\overset{C}{\underset{C}{C}}\overset{C}{\underset{C}{C}}—\underset{R}{C}—R$	1 × 10^4 per group. Generally in 0.006 cm. cell	IV

(*Continued on next page*)

Table VII. (*Continued*)

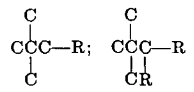
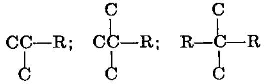
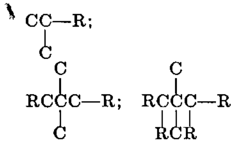
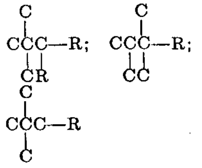
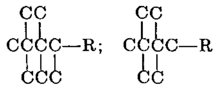
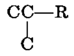
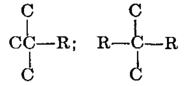
Band Position, μ and Cm.⁻¹	Structure	Intensity, E/Mole/Ml./Cm.	Table
7.98–8.10 1253–1235		2×10^4 per group. Generally in 0.006 cm. cell	IV
7.28–7.32 1374–1366		0.001 cm. or thinner cell. Intensity varies with group	III IV
7.23–7.26 1383–1377	CH_3	1.8×10^4 per CH_3 0.001 cm. or thinner cell	II
7.19–7.24 1391–1381		4×10^4 per group. 0.001 cm. or thinner cell	III V
7.14 7.18 1401–1393		$(2–5) \times 10^4$ per group. 0.001 cm. or thinner cell	IV V
7.10–7.12 1408–1404		3×10^4 per group 0.001 cm. or thinner cell	IV
6.75–7.0 1481–1430	General paraffinic	Observed in 0.001 cm. or thinner cell	
4.37–4.39 2290–2280		0.01×10^4 per carbon atom 40–50% T in 0.07 cm. cell	III
4.35–4.37 2300–2290		0.01×10^4 per carbon atom 30–50% T in 0.07 cm. cell	IV V

Table VIII. Correlations for Olefins

Most of the correlations given here have been described elsewhere (*2, 6, 11, 13, 15*). However, this presentation appears to provide a better starting point for applications in petroleum chemistry.

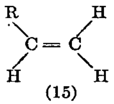
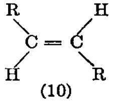
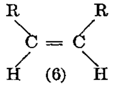
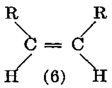
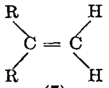
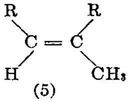
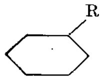
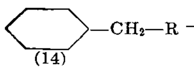
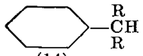
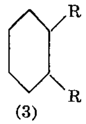
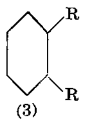
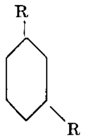
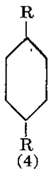
Structure	Band Position, μ and Cm.⁻¹	Intensity, E/Mole/Ml./Cm.	Remarks
 (15)	10.89–11.00 916–909	12×10^4 Approx. 30% T in 0.0008 cm. cell	Lowest intensity 10.9×10^4, highest 15.2×10^4
	9.96–10.09 1004–991	4.5×10^4 60–70% T in 0.0014 cm. cell	Lowest intensity 3.3×10^4, highest 5.7×10^4
	7.04–7.08 1420–1412	1.4×10^4 80–90% T in 0.0014 cm. cell	Lowest intensity 0.7×10^4, highest 2.3×10^4. Shoulder on side of 6.8 band therefore, intensity limits are wide
	6.08–6.10 1645–1639	3.7×10^4 60–70% T in 0.0014 cm. cell	Lowest intensity 2.8×10^4, highest 4.4×10^4
	5.46–5.54 1832–1805	0.57×10^4 30–40% T in 0.017 cm. cell	Lowest intensity 0.50×10^4, highest 0.67×10^4. cis olefins did not absorb here others irregular in this respect
	5.04–5.08 1984–1969	0.11×10^4 40–50% T in 0.073 cm. cell	Lowest intensity 0.07×10^4, highest 0.14×10^4
 (10)	10.22–10.37 979–964	10×10^4 20% T in 0.0009 cm. cell	Lowest intensity 9.2×10^4, largest 11.9×10^4. *cis*-3-hexene and *cis*-2-hexene interfere badly
	6.0 1667	0	Band is missing or very low in intensity. This correlates well with selection rule forbidding band in molecules symmetrical about C=C bond
 (6)	13.71–14.82 729–675	6×10^4 40–60% T in 0.0015 cm. cell	Intensity varies between 1.3×10^4 and 10.6×10^4
 (6) (*Contd.*)	7.00–7.16 1429–1397	20–40% T in 0.008 cm. cell	Intensity varies between 0.76×10^4 and 1.8×10^4
	6.02–6.13 1661–1631	0.9×10^4 20–40% T in 0.006 cm. cell	Lowest intensity 0.28, highest 1.3×10^4
 (7)	11.21–11.27 892–887	14×10^4 10–20% T in 0.0008 cm. cell	Intensity = $(12, 15, 16) \times 10^4$ on the three compounds measured. Many trans olefins absorb in this region; however, absorption is weaker
	6.02–6.10 1661–1639	3.8×10^4 60–70% in 0.0008 cm. cell	Intensities $(3.3, 4.2, 3.8) \times 10^4$ on 3 compounds
	5.58–5.61 1792–1783	0.52×10^4 60–70% in 0.0008 cm. cell	Intensity between $(0.42–1.65) \times 10^4$
	3.23–3.25 3096–3077	30–40% T in 0.007 cm. cell	Intensity between $(0.95–2.7) \times 10^4$
 (5)	12.01–12.38 833–808	4.0×10^4 20–40% T in 0.0013 cm. cell	Lowest intensity 3.3×10^4, largest 4.8×10^4
	10.8–11.01 926–908	0.8×10^4 20–40% T in 0.013 cm. cell	Lowest intensity 0.48×10^4, highest 1.2×10^4. Sometimes this band is accompanied by another of similar intensity at shorter wave lengths. This is not an impressive correlation
	5.91–6.00 1692–1667	0.57×10^4 40–60% T in 0.013 cm. cell	Lowest intensity 0.46×10^4, highest 0.68×10^4. This band is definitely at shorter wave lengths than 6-micron band in 1-olefins

Table IX. Structure and Associated Correlation Bands for Alkylbenzenes

Structure	Band Position, μ and Cm.$^{-1}$	Intensity, E/Mole/Ml./Cm.	Remarks
 (28)	14.27–14.40 701–694	20×10^4 0.0005 cm. cell	Sharp band in monoalkylbenzene spectra. Excluding toluene, range for monoalkylbenzenes is 14.27–14.35. When phenyl is on tertiary carbon, band generally appears near 14.29, while phenyl on secondary carbon generally causes absorption near 14.33; however, there is overlapping. Lowest intensity 11×10^4, highest 31×10^4
	11.00–11.15 909–897	0.9×10^4 0.005 cm. cell	In 3-phenyleicosane spectrum this band appears to be merged with another at 11.2 to give single maximum at 11.15. A fairly sharp band
	9.69–9.73 1032–1027	2×10^4 0.005 cm. cell	Six spectra submitted by National Aniline Co. (not included in this correlation) have band at 9.62. This band is most pronounced in spectra of low molecular weight compounds. Several polysubstituted benzenes have bands in or near this region (see Figure 7 and Table X). A sharp band. Lowest intensity 1.2×10^4, highest 3.9×10^4
	8.62–8.68 1160–1152	0.4×10^4 0.02 cm. cell	In three spectra submitted by National Aniline (not included in this correlation) band falls at shorter wave lengths than 8.62. Although weak, this band and that at 8.44 form a striking pair of sharp bands in spectra of higher molecular weight monoalkylbenzenes. Spectra of several polysubstituted benzenes exhibit bands in 8.62–8.68 range (see Figure 7 and Table X). In other spectra (*12, 14*) this is generally weak or moderately intense band. Lowest intensity 0.34×10^4, highest 0.84×10^4
	8.44–8.50 1184–1176	0.5×10^4 0.02 cm. cell	
 (14)	13.39–13.57 747–737	10×10^4 0.001 cm. cell	Well-defined band which makes very good correlation for this structure
 (14)	13.10–13.19 763–758	20×10^4 0.0005 cm. cell	Well-defined band giving good correlation
	11.21–11.31 892–884	0.3×10^4 0.02 cm. cell	Weak band sometimes on side of 11.0–11.15 band. Spectra of sec-butyl benzene and 1-methyl-1-phenylcyclobutane lack this band. In 2-phenyleicosane spectrum it appears to produce shoulder on 11.04 band, while in 3-phenyleicosane spectrum it apparently merges with band to give single maximum at 11.15. Spectra of some compounds with phenyl on secondary carbon atom also exhibit bands here, but this is not regular occurrence.
 (3)	13.20–13.55 760–740	10×10^4 0.001 cm. cell	Sharp bands. Bands in three *o*-alkylbenzene spectra lie between 13.25–13.46
	9.60–9.85 1040–1015	2×10^4 0.001 cm. cell	Bands sharp in three *o*-alkylbenzene spectra and lie between 9.69–9.79
 (3) (*Contd.*)	9.25–9.55 1080–1045	2×10^4 0.001 cm. cell	Bands sharp in three *o*-alkylbenzene spectra and lie between 9.33–9.50
	8.80–9.10 1135–1100	1×10^4 0.005 cm. cell	Bands sharp in *o*-alkylbenzene spectra. Lie between 8.85–9.04. Also sharp in other spectra (*12, 14*)
 (4)	14.15–14.50 710–690	10×10^4 0.001 cm. cell	Several spectra from (*12, 14*) have more than one band in 13.7–14.8 range. In four *m*-alkyl-benzene spectra band comes in range 14.21–14.45
	12.45–13.05 800–770	10×10^4 0.001 cm. cell	*m*-alkylbenzene bands lie in range 12.50–13.00
	11.15–11.65 895–860	2×10^4 0.005 cm. cell	This band and the one at 10.75–11.35 form a prominent sharp pair in spectra of four *m*-alkylbenzenes. Other spectra (*12, 14*) are in fair agreement with this band, but some Sadtler spectra are too mediocre to be definite. Pairing with 10.75–11.35 is not distinctive in most Sadtler spectra (*12*).
	10.75–11.35 930–880	1×10^4 0.005 cm. cell	See note above. This band included because it pairs with 11.15–11.65 to form a striking pair in *m*-alkylbenzene spectra
	9.45–9.70 1060–1030	1×10^4 0.005 cm. cell	Very sharp bands in alkylbenzene spectra lying between 9.52–9.62. Other spectra (*12, 14*) in fair agreement, but several have more than one band in this range. Bands sharp in other spectra (*12, 14*) also
	8.95–9.20 1120–1085	1×10^4 0.005 cm. cell	Sharp band in alkylbenzene spectra in range 9.04–9.12. Spectra of Sadtler compounds with meta substitution generally show one or more sharp bands in 9.1–9.4 range
	8.45–8.70 1185–1150 8.35–8.65 1200–1155	1×10^4 0.005 cm. cell	Distinctive pair in spectra of *m*-alkylbenzenes. Pairing is not distinctive in other spectra (*12, 14*)
 (4)	12.00–12.35 833–810	20×10^4 0.0005 cm. cell	*p*-alkylbenzene bands lie in range 12.08–12.27
	9.70–9.90 1030–1010	1×10^4 0.005 cm. cell	*p*-alkylbenzene spectra have sharp bands in range 9.77–9.85. Other spectra (*12, 14*) would be included in 9.6–10.0 range. Bands in other spectra (*12, 14*) are sharp
	9.35–9.65 1070–1035	2×10^4 0.005 cm. cell	*p*-alkylbenzene spectra have bands in range 9.40–9.58. Bands in *p*-alkylbenzene spectra are sharp except in one spectrum, where overlapping is apparent
	8.85–9.15 1130–1090	2×10^4 0.005 cm. cell	Sharp band in *p*-alkylbenzene spectra. Some other spectra (*12, 14*) exhibit more than one band in range, but most prominent band in these spectra is sharp
	8.30–8.50 1205–1175	0.5×10^4 0.02 cm. cell	This band and one at 8.15–8.35 form striking sharp pair in *p*-alkylbenzene spectra. Pairing is not distinctive in other spectra (*12, 14*)

(*Continued on next page*)

Table IX. (*Continued*)

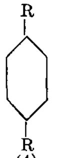
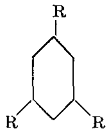
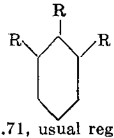
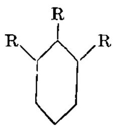
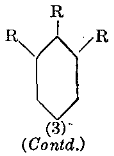
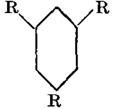
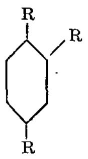
Structure	Band Position μ and Cm.⁻¹	Intensity, E/Mole/Ml./Cm.	Remarks
 (4) (*Contd.*)	8.15–8.35 1230–1195	0.5 × 10^4 0.02 cm. cell	Not distinctive in other spectra (*12*, *14*) but included because it pairs with 8.30–8.50 in alkylbenzene spectra
	6.58–6.62 1521–1510	10 × 10^4 0.001 cm. cell	Range for alkylbenzene spectra has not been adjusted as for bands at wave lengths longer than 7 microns. Band is definitely at shorter wave lengths than in other alkylbenzene spectra (see Figure 7 and Table X). Barnes (*4*) makes similar observation
	6.04–6.12 1656–1633	0.5 × 10^4 0.005 cm. cell	Range not adjusted as for bands at wave length longer than 7 microns. Colthup (*5*) states that the "1620 cm.⁻¹ band in spectra of para substituted benzenes is variable in intensity but is strongest when one group is ortho-para directing and other meta directing." Most alkylaromatics absorb at longer wave lengths (near 6.2). *p*-alkylbenzene spectra are clear at 6.2, but this band at shorter wave lengths is striking
 (2)	14.30–14.65 700–680	5 × 10^4 0.001 cm. cell	
	11.75–12.05 850–830	20 × 10^4 0.0005 cm. cell	
	11.15–11.40 895–880	1 × 10^4 0.02 cm. cell	
	9.55–9.70 1045–1030	2 × 10^4 0.001 cm. cell	
	8.50–8.65 1175–1155	0.5 × 10^4 0.02 cm. cell	Bands in both alkylbenzene spectra come at 8.58.
	6.77–6.85 1478–1460	5 × 10^4 0.001 cm. cell	Alkylbenzenes with this structure and structure  have no bands at 6.67–6.71, usual region for absorption in alkylbenzenes. Limits are positions of bands in the two spectra
 (3)	13.40–14.15 745–705	5 × 10^4 0.001 cm. cell	Bands in spectra of alkylbenzenes with this substitution are in range 13.47–14.10 Sharp band in these spectra
	12.80–13.15 780–760	10 × 10^4 0.001 cm. cell	Observed in range 12.89–13.06 in pertinent alkylbenzene spectra. Sharp band in these spectra
 (3) (*Contd.*)	10.00–10.20 1000–980	1 × 10^4 0.005 cm. cell	Three pertinent alkylbenzene spectra have band in range 10.06–10.15, but others fall near these bands and it is not clear which are true correlation bands
	9.65–9.95 1040–1000	1 × 10^4 0.005 cm. cell	Three pertinent alkylbenzene spectra absorb in range, but two bands occur in one of these spectra
	9.25–9.50 1080–1050	1 × 10^4 0.005 cm. cell	This band included because it comes between 9.65–9.45 and 9.00–9.20 bands in three pertinent alkylbenzene spectra
	9.00–9.20 1110–1085	1 × 10^4 0.005 cm. cell	Sharp band in three pertinent alkylbenzene spectra
	8.50–8.65 1175–1160	1 × 10^4 0.005 cm. cell	Sharp band in three pertinent alkylbenzene spectra
	7.95–8.10 1260–1240	0.5 × 10^4 0.02 cm. cell	Sharp band in three pertinent alkylbenzene spectra. While not strong, it stands out in these spectra
	6.77–6.85 1478–1468	10 × 10^4 0.001 cm. cell	Spectra of three pertinent alkylbenzenes are clear at 6.67–6.71, range in which alkylbenzenes generally absorb See also 
	6.27–6.29 1549–1591	1 × 10^4 0.02 cm. cell	This band is definitely at longer wave lengths in spectra of three alkylbenzenes with this structure than in spectra of other alkyl benzenes (6.19–6.27)
 (4)	12.15–12.45 825–805	10 × 10^4 0.001 cm. cell	Bands sharp in spectra of alkylbenzenes with this structure
	11.30–11.50 885–870	2 × 10^4 0.005 cm. cell	Bands sharp in spectra of pertinent alkylbenzenes
	9.80–10.10 1020–990	1 × 10^4 0.005 cm. cell	Many other spectra (*12*, *14*) which fit this correlation have only weak bands in this range
	9.55–9.85 1045–1015	2 × 10^4 0.005 cm. cell	Some weak bands in other spectra (*12*, *14*) used in checking this correlation
	8.80–8.95 1135–1120	1 × 10^4 0.005 cm. cell	
	8.60–8.75 1165–1145	1 × 10^4 0.02 cm. cell	Bands in pertinent alkylbenzene spectra are sharp
	8.20–8.35 1220–1195	0.5 × 10^4 0.02 cm. cell	Bands in pertinent alkylbenzene spectra are sharp
	6.17–6.19 1620–1617	1 × 10^4 0.001 cm. cell	In spectra of four alkylbenzenes with this structure this band is at shorter wave lengths than 6.19–6.27 region characteristic of alkylbenzenes in general. This close separation may not hold in light of more data

Table X. Correlation Bands and Their Associated Structures for Alkylbenzenes

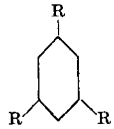
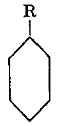
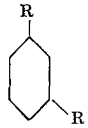
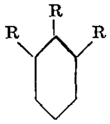
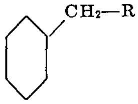
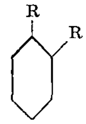
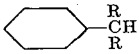
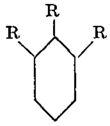
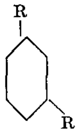
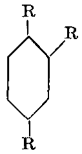
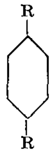
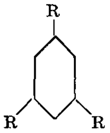
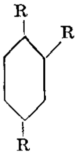
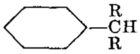
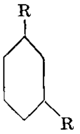
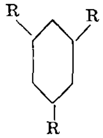
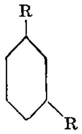
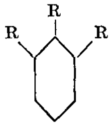
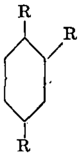
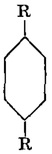
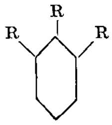
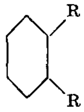
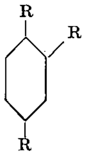
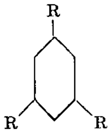
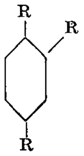
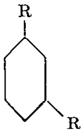
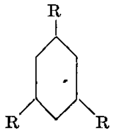
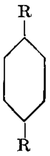
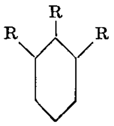
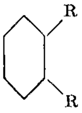
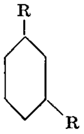
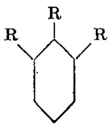
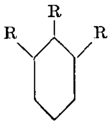
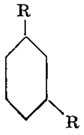
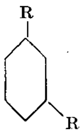
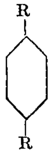
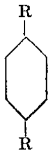
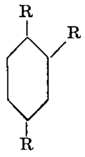
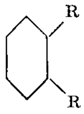
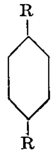
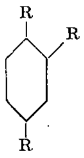
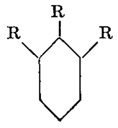
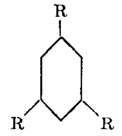
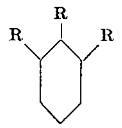
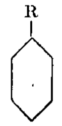
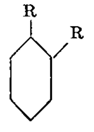
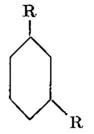
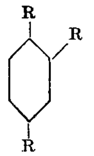
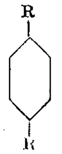
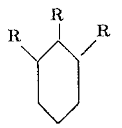
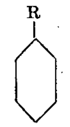
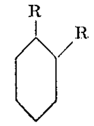
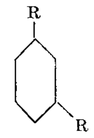
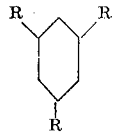
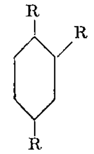
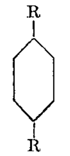
Band Position[a], μ and Cm.$^{-1}$	Structure	Intensity, E/Mole/Ml./Cm.
14.30-14.65 700-680		5×10^4 0.001 cm. cell
14.27-14.40 701-694		20×10^4 0.0005 cm. cell
14.15-14.50 710-690		10×10^4 0.001 cm. cell
13.40-14.15 745-705		5×10^4 0.001 cm. cell
13.39-13.57 747-737		10×10^4 0.001 cm. cell
13.20-13.55 760-740		10×10^4 0.001 cm. cell
13.10-13.19 763-758		20×10^4 0.0005 cm. cell
12.80-13.15 780-760		10×10^4 0.001 cm. cell
12.45-13.05 800-770		10×10^4 0.001 cm. cell
12.15-12.45 825-805		10×10^4 0.001 cm. cell
12.00-12.35 833-810		20×10^4 0.0005 cm. cell
11.75-12.05 870-830		20×10^4 0.0005 cm. cell
11.30-11.50 885-870		2×10^4 0.005 cm. cell
11.21-11.31 892-884		0.3×10^4 0.02 cm. cell
11.15-11.65 895-860		2×10^4 0.005 cm. cell
11.15-11.40 895-880		1×10^4 0.02 cm. cell
11.00-11.15 909-897		0.9×10^4 0.005 cm. cell
10.75-11.35 930-880		1×10^4 0.005 cm. cell
10.00-10.20 1000-980		1×10^4 0.005 cm. cell
9.80-10.10 1020-990		1×10^4 0.005 cm. cell
9.70-9.90 1030-1010		1×10^4 0.005 cm. cell
9.69-9.73 1032-1027		2×10^4 0.005 cm. cell
9.65-9.95 1035-1005		1×10^4 0.005 cm. cell
9.60-9.85 1040-1015		2×10^4 0.001 cm. cell

Table X. (*Continued*)

Band Position[a], μ and Cm.$^{-1}$	Structure	Intensity, E/Mole/Ml./Cm.	Band Position[a], μ and Cm.$^{-1}$	Structure	Intensity, E/Mole/Ml./Cm.
9.55–9.85 1045–1015		2 × 10^4 0.005 cm. cell	8.62–8.68 1160–1152		0.4 × 10^4 0.02 cm. cell
9.55–9.70 1045–1030		2 × 10^4 0.001 cm. cell	8.60–8.75 1165–1145		1 × 10^4 0.02 cm. cell
9.45–9.70 1060–1030		1 × 10^4 0.005 cm. cell	8.50–8.65 1175–1155		0.5 × 10^4 0.02 cm. cell
9.35–9.65 1070–1035		2 × 10^4 0.005 cm. cell	8.50–8.65 1175–1160		1 × 10^4 0.005 cm. cell
9.25–9.55 1080–1045		2 × 10^4 0.001 cm. cell	8.45–8.70 1185–1150		1 × 10^4 0.005 cm. cell
9.25–9.50 1080–1050		1 × 10^4 0.005 cm. cell	8.44–8.50 1184–1176		0.5 × 10^4 0.02 cm. cell
9.00–9.20 1110–1085		1 × 10^4 0.005 cm. cell	8.35–8.65 1200–1155		1 × 10^4 0.005 cm. cell
8.95–9.20 1120–1085		1 × 10^4 0.005 cm. cell	8.30–8.50 1205–1175		0.5 × 10^4 0.02 cm. cell
8.85–9.15 1130–1090		2 × 10^4 0.005 cm. cell	8.20–8.35 1220–1195		0.5 × 10^4 0.02 cm. cell
8.80–9.10 1135–1100		1 × 10^4 0.005 cm. cell	8.15–8.35 1230–1200		0.5 × 10^4 0.02 cm. cell
8.80–8.95 1135–1120		1 × 10^4 0.005 cm. cell	7.95–8.10 1260–1240		0.5 × 10^4 0.02 cm. cell

(*Continued on page 332*)

Table X. (*Continued*)

Band Position[a], μ and Cm.⁻¹	Structure	Intensity, E/Mole/Ml./Cm.
6.77–6.85 1478–1460		5 × 10^4 0.001 cm. cell
		
6.66–6.71 1501–1490		10 × 10^4 0.001 cm. cell
6.63–6.65 1509–1504		10 × 10^4 0.001 cm. cell
		
		
6.58–6.62 1521–1510		10 × 10^4 0.001 cm. cell
6.27–6.29 1594–1591		1 × 10^4 0.02 cm. cell
6.19–6.27 1617–1594		2 × 10^4 0.001 cm. cell
		
		
		
6.17–6.19 1620–1617		1 × 10^4 0.001 cm. cell
6.04–6.12 1656–1633		0.5 × 10^4 0.005 cm. cell

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[a] Most reliable and useful correlations are underlined. For monoalkylbenzene structures ranges are between the maximum and minimum observed wave lengths. For polyalkylbenzene structures ranges are greater. They are rounded values obtained by adding between 0.05 and 0.10 micron to longest observed wave length and subtracting a like amount from the shortest.

ever, this chart is meant to apply regardless of the type of substituent (7).

Although only a few spectra of any single type of polyalkylbenzene are available, their correlation bands can be identified by comparing their spectra with Colthup's chart. However, the ranges given by Colthup are much wider than found in the observed spectra, just as they are for the monoalkylbenzene substitution. Therefore, the ranges given in Tables IX and X for the polyalkylbenzene structures are narrower than called for by Colthup's chart. However, those beyond 7 microns were made wider than the maximum and minimum wave lengths observed in the available spectra in order to encompass safely the positions of the bands in the spectra of all pertinent compounds, unknown as well as known. The wave-length ranges given for each correlation band are rounded values obtained by

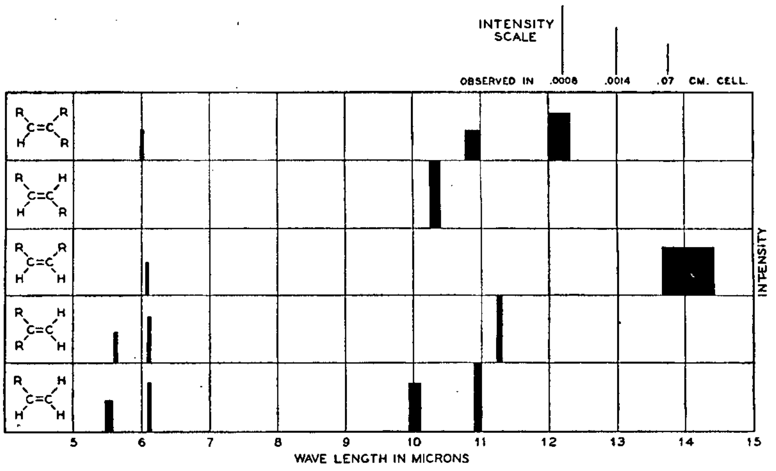

Figure 6. Correlation Bands for Olefinic Structures

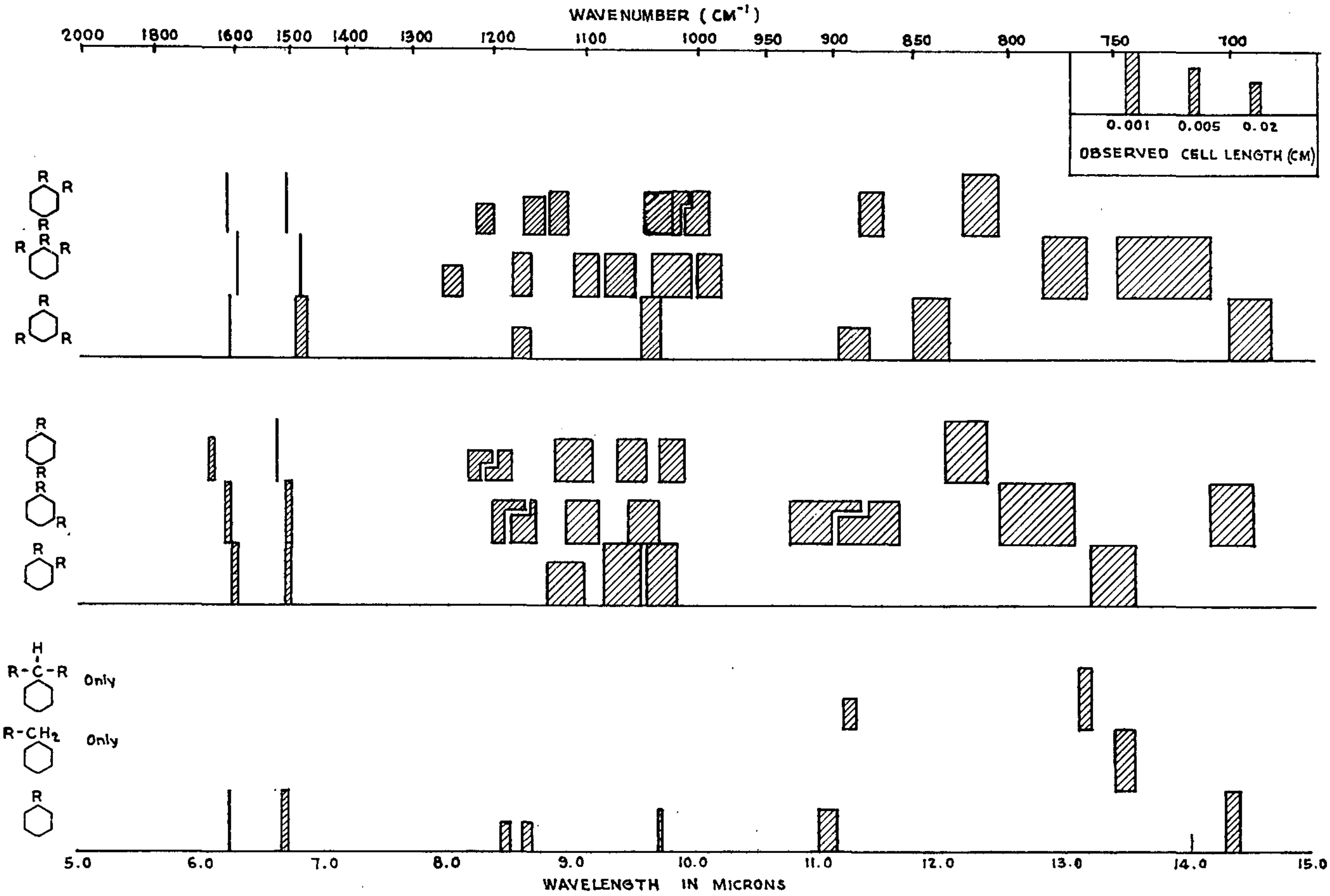

Figure 7. Correlations for Alkylbenzene Structures

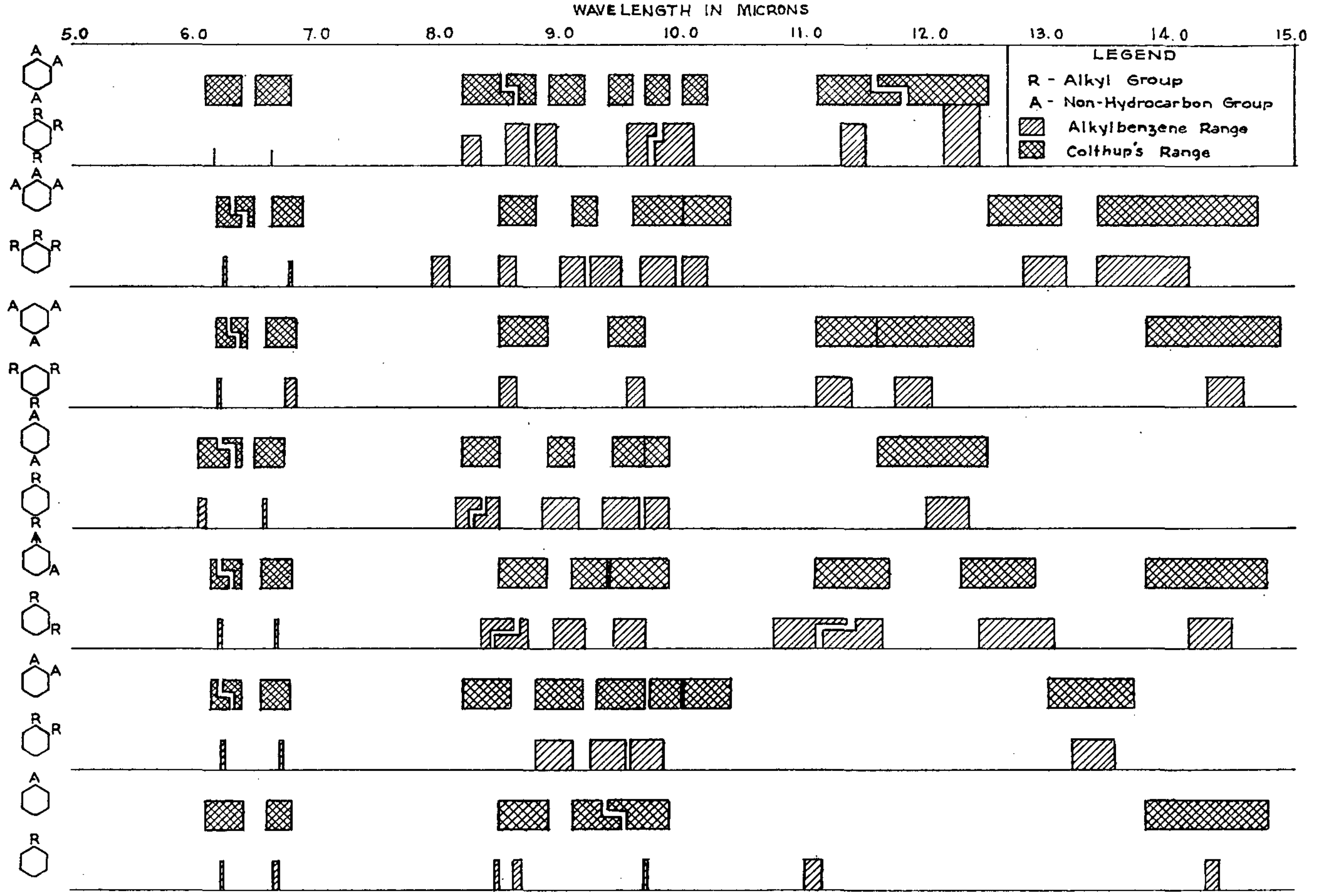

Figure 8. Comparison of Correlations Determined from Alkylbenzene Spectra Only and All Substituted Benzene Spectra

adding between 0.05 and 0.10 micron to the longest observed wave length and subtracting a similar amount from the shortest.

Table IX lists the structures and gives their correlation bands, band intensities, and remarks about the properties of the bands. Table X is the inverse of Table IX but includes some bands not in Table IX which are common to all alkylbenzene spectra.

Figure 7 charts the correlations. Figure 8 compares the ranges given here with those of Colthup. Some bands given by Colthup were not found in the alkylbenzene spectra or in the spectra in the Sadtler catalog (*12*).

Recently Young, Du Vall, and Wright have related the structures of the bands between 5 and 6 microns to the type of ring substitution (*16*). These results have been found to apply without change to the alkylbenzenes.

ACKNOWLEDGMENT

The authors are indebted to D. C. Smith for providing them with results from his studies which, in many cases, paralleled their own work.

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Infrared Absorption Band Due to Nitrile Stretching Vibration

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In the course of measurement of the infrared absorption spectra of some unsaturated dinitriles, it was observed that the strong band at ca. 2250 cm.$^{-1}$ due to the stretching of the $C{\equiv}N$ bond was split, in some cases, into a doublet. The nitrile stretching frequency of about 70 nitriles was studied in an effort to explain this behavior. The nitrile stretching band was found to occur at 2250 ± 10 cm.$^{-1}$ in saturated nitriles or in olefinic nitriles wherein no conjugation exists between the nitrile and olefinic groups. In conjugated nitriles, the band is shifted to 2225 ± 8 cm.$^{-1}$ In dinitriles containing both types of groups, both bands are found. Aromatic nitriles in which the nitrile is attached to the ring have an intermediate nitrile stretching frequency, the exact value depending on the nature of other substituents on the ring. Thus the study of the nitrile band in a compound of unknown structure permits some conclusions to be drawn as to the relations between the nitrile group and other parts of the molecule.

IN THE course of measurement of the infrared adsorption spectra of some unsaturated dinitriles, it was observed that the strong band at approximately 2250 cm.$^{-1}$ due to the stretching of the $C{\equiv}N$ bond was split, in some cases, into a doublet which just could be resolved with the sodium chloride optics being used. The splitting always occurred when the two nitrile groups in the molecule differed in their relation to the olefinic bond—i.e., one group was conjugated with the double bond while the other was not. If both groups were conjugated or unconjugated, the usual single sharp band appeared.

Reitz and Sabathy (*1*, *2*) and Reitz and Skrabel (*3*) have studied the nitrile stretching frequency of a Raman shift of a number of mononitriles. The former authors (*2*) observed that conjugation of an olefinic group with the nitrile group caused a shift in the $C{\equiv}N$ frequency. They report the Raman shift occurs at 2245 cm.$^{-1}$ in aliphatic nitriles, at 2229 cm.$^{-1}$ in aromatic compounds, and at 2220 cm. $^{-1}$ in conjugated compounds. No similar work has been reported on the infrared absorption of the nitrile group. Consequently, the nitrile stretching frequency of a large number of nitrile compounds was measured on an infrared spectrometer to determine whether or not the shifts in Raman spectra, due to conjugation of the nitrile group with an olefinic double bond, could be substantiated by infrared data.

The authors have found that the nitrile stretching frequency in saturated nitriles, or in unsaturated nitriles in which no conjugation exists, occurs at 2250 ± 10 cm.$^{-1}$ In unsaturated nitriles in which conjugation does exist between the nitrile group and an olefinic double bond, the band is found at 2225 ± 7 cm.$^{-1}$ Dinitriles having both types of group have both bands. Aromatic nitriles in which the nitrile is attached to the ring have an intermediate nitrile stretching frequency, the exact value depending on the nature of other substituents on the ring. Thus, by a study of the exact position of the nitrile band in an unknown compound, the relation of the nitrile group to any unsaturated groups can be established.

In the course of this work, it was noted that the intensity of the nitrile absorption varied considerably. In nitriles containing only carbon and hydrogen in addition to the nitrile group(s), the band is usually intense. However, as electronegative groups, particularly those containing oxygen, are introduced into the molecule, the band becomes weaker. When the carbon atom bonded to the nitrile group is also bonded to an electronegative group, the nitrile stretching frequency is very weak or absent.

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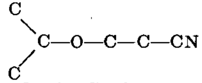
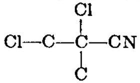
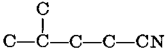
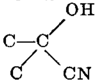
Table I. Nitrile Stretching Frequency of Some Aliphatic Mononitriles

Compound	Formula[a]	Source[b]	C≡N Frequency, Cm.$^{-1}$
Acetonitrile	C—CN	E.K. No. 488[c]	2254
Propionitrile	C—C—CN	Genesee[c]	2249
β-Chloropropionitrile	Cl—C—C—CN	M. No. 6227	2260
β-Bromopropionitrile	Br—C—C—CN	Sapon	2258
β-Isopropoxypropionitrile	 $\mathrm{(C)_2C{-}O{-}C{-}C{-}CN}$	Am. Cy. Co.	2254
β-Hydroxypropionitrile	HO—C—C—CN	M. No. 6367	2256
2,3-Dichloro-2-methylpropionitrile	 $\mathrm{Cl{-}C{-}C(Cl)(C){-}CN}$	Du Pont	2244 (R)[d]
n-Butyronitrile	C—C—C—CN	E.K. No. 741[c]	2253
4-Chlorobutyronitrile	Cl—C—C—C—CN	Sapon	2253
4-Bromobutyronitrile	Br—C—C—C—CN	Sapon	2252
n-Valeronitrile	C—C—C—C—CN	Sapon	2254
5-Bromovaleronitrile	Br—C—C—C—C—CN	Sapon	2249
Isocapronitrile	 $\mathrm{C{-}C(C){-}C{-}C{-}CN}$	E.K. No. 65	2249
6-Aminocapronitrile	H_2N—C—C—C—C—C—CN	Du Pont	2252
n-Heptanonitrile	$C{-}(C)_5{-}CN$	Sapon	2250
Nonanonitrile (*n*-octyl cyanide)	$C{-}(C)_7{-}CN$	Sapon	2250
Undecanonitrile (*n*-decyl cyanide)	$C{-}(C)_9{-}CN$	Sapon	2250
Pentadecanonitrile	$C_{14}H_{30}CN$	Sapon	2250
Heptadecanonitrile (cetyl cyanide)	$C_{16}H_{34}CN$	Sapon	2249
Acetone cyanohydrin	 $\mathrm{C{-}C(OH)(C)(CN)}$	M. No. 6655	2246

[a] For simplicity, only carbon skeletal formula is given.
[b] E.K. = Eastman Kodak Co., Rochester, N. Y.
M = Matheson Co., Inc., East Rutherford, N. J.
Sapon = Sapon Laboratories, Brooklyn, N. Y.
Du Pont = E. I. du Pont de Nemours & Co., Inc., Wilmington, Del. (used to identify both commercial and laboratory preparations).
Genesee = Genesee Research Corp., Rochester, N. Y.
Am. Cy. Co. = American Cyanamid Co., New York, N. Y
[c] Redistilled before use.
[d] Raman shift. Band too weak to measure in infrared.

EXPERIMENTAL

Infrared absorption measurements were made with a Perkin-Elmer Model 12-C spectrometer. A lithium fluoride prism was used to obtain the necessary resolution for this work. The wavelength calibration was made by comparison with the rotational fine structure of the carbon monoxide and carbon dioxide bands at 2046 to 2225 cm.$^{-1}$ and 2292 to 2347 cm.$^{-1}$

Liquid samples were run directly in 0.025-mm. sodium chloride cells or as solutions in suitable solvents in 0.050-mm. cells. Solids were run as solutions in suitable solvents, as Nujol suspensions, or as films melted onto salt plates.

The nitrile samples were assembled from a variety of sources, as shown in Tables I to IV. Some of the commercial samples were subjected to further purification before measurement. Many of the unusual unsaturated nitriles were prepared in the laboratory. In all such cases, the structure of the sample was proved by suitable independent techniques before their inclusion in this work.

EXPERIMENTAL RESULTS

The results obtained are summarized in Tables I to V. Except for acetonitrile and fumaronitrile, none of the compounds showed any absorption bands in the region scanned (2281 to 2146 cm.$^{-1}$) other than those listed.

DISCUSSION OF RESULTS

The saturated mono- and dinitriles listed in Tables I and II (excluding malononitrile) have an average frequency of 2250 ± 10 cm.$^{-1}$ The 17 compounds listed in Table III having a nitrile group unconjugated with the olefinic double bond show the band at 2252 ± 11 cm.$^{-1}$ (It is doubtful that the difference between the two averages is significant.)

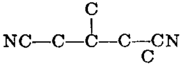
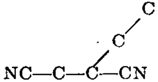
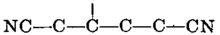
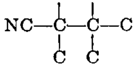
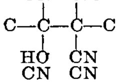
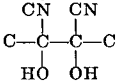
The 12 compounds in Table III having one or more nitriles conjugated with the double bond (excluding fumaronitrile) have a strong band at 2225 ± 7 cm.$^{-1}$ Only 4 compounds having both types of nitrile group were available, but, as expected, they all show both bands.

Examination of the data for the various substituted propionitriles listed in Table I suggests that the nitrile frequency is shifted slightly to lower wave lengths by substitution of electronegative groups on the beta-carbon. This shift is not nearly so pronounced as that due to conjugation, but it may be of some significance. Study of more compounds of this type will be necessary to establish this point.

Table IV shows the data obtained for some aromatic nitriles. As expected, the behavior is about the same as with aliphatic nitriles. Compounds having the nitrile group attached to the aromatic nucleus show the low frequency, while insertion of one or two methylene groups between the ring and the nitrile group causes the frequency to shift to the higher value.

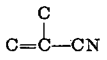
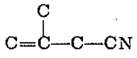
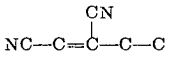
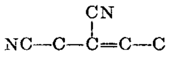
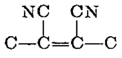
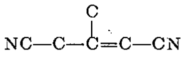
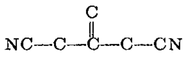
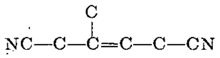
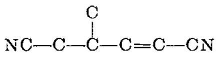
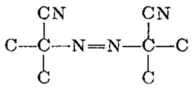
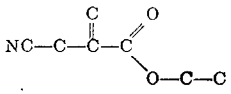
Since the unsaturation in the aromatic ring is not equivalent to olefinic unsaturation, it is not surprising to find that most of the compounds examined showed bands at slightly higher frequencies than the conjugated olefinic compounds. In substi-

Table II. Nitrile Stretching Frequency of Some Aliphatic Dinitriles

Compound	Formula[a]	Source[a]	C≡N Frequency Cm.$^{-1}$
Malononitrile	NC—C—CN	M. No. 6660	2278
Succinonitrile	NC—C—C—CN	Sapon	2261
Glutaronitrile	NC—C—C—C—CN	Sapon	2254
Adiponitrile	NC—C—C—C—C—CN	Du Pont	2248
β-Methylglutaronitrile	 $\mathrm{NC{-}C{-}C(C){-}C{-}CN}$	Du Pont	2247
Ethylsuccinonitrile	 $\mathrm{NC{-}C{-}C(C{-}C){-}CN}$	Du Pont	2247
Pimelonitrile	$NC{-}(C)_5{-}CN$	Sapon	2248
β-Methyladiponitrile	 $\mathrm{NC{-}C{-}C(C){-}C{-}C{-}CN}$	Du Pont	2249
Suberonitrile	$NC{-}(C)_6{-}CN$	Sapon	2249
Tetramethylsuccinononitrile	 $\mathrm{NC{-}C(C)_2{-}C(C)_2{-}CN}$	Du Pont	2243
Azeleonitrile	$NC{-}(C)_7{-}CN$	Sapon	2249
Sebaconitrile	$NC{-}(C)_8{-}CN$	Sapon	2249
DL-Biacetylcyanohydrin	 $\mathrm{C{-}C(CN)(HO){-}C(OH)(CN){-}C}$	Du Pont	2259
meso-Biacetylcyanohydrin	 $\mathrm{C{-}C(CN)(HO){-}C(CN)(OH){-}C}$	Du Pont	2259

[a] See Table I.

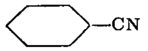
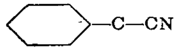
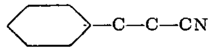
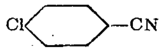
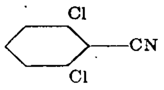
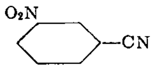
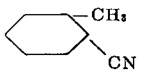
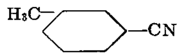
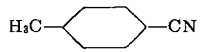
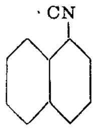
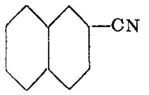
Table III. Nitrile Stretching Frequency of Some Unsaturated Nitriles

Compound[a]	Formula[b]	C≡N Frequency, Cm.$^{-1}$	
		Conjugated	Non-conjugated
Acrylonitrile	$\mathrm{C{=}C{-}CN}$	2230	..
Methacrylonitrile	 $\mathrm{C{=}\overset{\overset{C}{\vert}}{C}{-}CN}$	2230	..
Vinylacetonitrile (allyl cyanide)	$\mathrm{C{=}C{-}C{-}CN}$	..	2253
cis-1-Cyano-1-propene	$\mathrm{C{-}C{=}C{-}CN}$	2221	..
trans-1-Cyano-1-propene	$\mathrm{C{-}C{=}C{-}CN}$	2223	..
trans-1-Cyano-2-butene	$\mathrm{C{-}C{=}C{-}C{-}CN}$	..	2253
3-Cyano-2-methyl-1-propene	 $\mathrm{C{=}\overset{\overset{C}{\vert}}{C}{-}C{-}CN}$	..	2252
1-Cyano-1,3-butadiene	$\mathrm{NC{-}C{=}C{-}C{=}C}$	2217	..
Fumaronitrile	$\mathrm{NC{-}C{=}C{-}CN}$	2242 2271 (weak)	..
cis-1,4-Dicyano-1-butene	$\mathrm{NC{-}C{=}C{-}C{-}C{-}CN}$	2224	2249
trans-1,4-Dicyano-2-butene	$\mathrm{NC{-}C{-}C{=}C{-}C{-}CN}$	..	2257
1,2-Dicyano-1-butene	 $\mathrm{NC{-}C{=}\overset{\overset{CN}{\vert}}{C}{-}C{-}C}$	2233	
1,2-Dicyano-2-butene	 $\mathrm{NC{-}C{-}\overset{\overset{CN}{\vert}}{C}{=}C{-}C}$	2225	2258
2,3-Dicyano-2-butene	 $\mathrm{C{-}\overset{\overset{NC}{\vert}}{C}{=}\overset{\overset{CN}{\vert}}{C}{-}C}$	2231	..
1,3-Dicyano-2-methyl-1-propene	 $\mathrm{NC{-}C{-}\overset{\overset{C}{\vert}}{C}{=}C{-}CN}$	2226	2258
2-(Cyanomethyl)-3-cyano-1-propene	 $\mathrm{NC{-}C{-}\overset{\overset{C}{\Vert}}{C}{-}C{-}CN}$	..	2257
1,4-Dicyano-2-methyl-2-butene	 $\mathrm{NC{-}C{-}\overset{\overset{C}{\vert}}{C}{=}C{-}C{-}CN}$	..	2254
1,4-Dicyano-3-methyl-1-butene	 $\mathrm{NC{-}C{-}\overset{\overset{C}{\vert}}{C}{-}C{=}C{-}CN}$	2220	2258
1,6-Dicyano-2,4-hexadiene	$\mathrm{NC{-}C{-}C{=}C{-}C{=}C{-}C{-}CN}$	..	2253
α,α′-Azobisisobutylnitrile	 $\mathrm{C{-}\underset{\underset{C}{\vert}}{\overset{\overset{CN}{\vert}}{C}}{-}N{=}N{-}\underset{\underset{C}{\vert}}{\overset{\overset{CN}{\vert}}{C}}{-}C}$	..	2243
Ethyl-2-cyanomethylacrylate	 $\mathrm{NC{-}C{-}\overset{\overset{C}{\Vert}}{C}{-}C({=}O){-}O{-}C{-}C}$	..	2256

[a] Except for allyl cyanide (E.K. No. 3182) all materials were obtained within Du Pont Co. A number are commercially available from other sources.

[b] See Table I.

Table IV. Nitrile Stretching Frequency of Some Aromatic Nitrile

Compound	Formula[a]	Source[a]	C≡N Frequency, Cm.$^{-1}$	
			Conjugated	Nonconjugated
Benzonitrile		E.K. No. 487[b]	2230	..
Phenylacetonitrile		E.K. No. 203[b]	..	2254
β-Phenylpropionitrile		E.K. No. 3242	..	2248
p-Chlorobenzonitrile		Du Pont	2230	..
2,5-Dichlorobenzonitrile		Genesee	2238	..
m-Nitrobenzonitrile		Genesee	2240	..
p-Nitrobenzonitrile		Genesee	2238	..
p-Aminobenzonitrile		Du Pont	2221	..
o-Toluonitrile		M. No. 6557	2227	..
m-Toluonitrile		M. No. 6558	2232	..
p-Toluonitrile		M. No. 6559	2231	..
Terephthalonitrile		Du Pont	2236	..
1-Naphthonitrile		Genesee	2224	..
2-Naphthonitrile		Genesee	2230	..

[a] See Table I.

[b] Redistilled before use

tuted benzonitriles in which the substituents tend to reduce the electron density in the benzene ring and, consequently, the bond force constants so that the aromatic nucleus appears less unsaturated (as in the nitrobenzonitriles), the nitrile frequency is shifted toward the saturated value. When substituents are present which increase the electron density (as in aminobenzonitrile) the opposite effect is noted. Additional work on substituted benzonitriles should be most interesting.

Table V. Intensity of C≡N Stretching Frequency

Compound	Intensity[a]
Acetonitrile	0.25
Acrylonitrile	0.30
β-Chloropropionitrile	0.26
Heptanonitrile	0.33
Heptadecanonitrile	0.24
Adiponitrile	0.31
Acetone cyanohydrin	0.09

[a] $\text{Intensity} = \frac{\text{absorbancy (0.25 mm. cell)}}{\text{mg. CN/ml. } CCl_4}$

The importance of these observations seems obvious: By measurement of the exact frequency of the nitrile stretching band, the analyst can quickly establish the relation of the nitrile group to the rest of the molecule. If the band falls at ca. 2250 cm.$^{-1}$, the nitrile group is probably in a saturated compound or in a position in an olefinic compound unconjugated to the double bond. The presence of the band at 2225 cm.$^{-1}$ indicates conjugation with an olefinic double bond. If the band falls outside one of these two ranges, some conclusions can be drawn as to the nature of the compound. If the band is between these ranges, it is almost certainly associated with an aromatic grouping or with some form of conjugation which is less effective than straight conjugation. Similarly, if the band is below 2220 cm.$^{-1}$, the nitrile may be part of a conjugation system which is more effective than a single double bond.

The intensity of the nitrile absorption band varies somewhat. In nitriles containing only carbon, hydrogen, and nitrogen the band is usually intense, and its strength is a function of the proportion of the nitrile group to the total molecule. A number of compounds were examined, however, in which the nitrile band was weak or completely absent. These compounds usually contained oxygenated groups. The "quenching" effect was greatest when the oxygenated group was attached to the same carbon as the nitrile group. In only one case were compounds differing only in their oxygenated groups available. The nitrile band in DL- and in meso-biacetylcyanohydrin was weak, though detectable. In the corresponding acetoxy compounds, however, the band could not be found although the method of synthesis, the chemical analysis, and the chemical reactions for the samples indicated them to contain nitrile groups. Quantitative measurements made on some typical nitriles are included in Table V to illustrate this behavior.

Quantitative functional group analysis using the nitrile stretching band should be done with some caution. If the nitriles in the sample are all of the same type, the determination can be carried out without difficulty. If, however, both conjugated and unconjugated nitrile groups are present in the sample, as in a mixture of propio- and acrylonitrile, care must be used to ensure that the analytical conditions used either resolve the two nitrile bands or quantitatively sum them. Similarly, care should be used that the intensity of the nitrile band is constant for the compounds being determined.

SUMMARY

The study of the nitrile stretching frequency of a series of saturated nitriles has shown the band to occur at 2250 ± 10 cm.$^{-1}$ The band occurs at essentially this same frequency in unsaturated nitriles in which no conjugation exists between the nitrile and olefinic groups. In conjugated nitriles, however, the band is shifted to 2225 ± 8 cm.$^{-1}$ In dinitriles containing both types of groups, both bands are found.

The band is found at an intermediate position in aromatic compounds having the nitrile group attached to the nucleus. Its exact position in these compounds depends on the nature of other substituents on the ring.

A study of the exact position of the nitrile band, therefore, will permit the analyst to establish, at least in part, the relation between the nitrile group and an unsaturated group or groups in the molecule.

The nitrile band is usually very intense, except in compounds containing oxygenated groups. Compounds that have oxygenated groups attached to the same carbon atom as the nitrile group show a marked decrease in intensity, or even complete absence of the nitrile band.

In view of these observations, some care must be used in making quantitative functional group analysis based on the nitrile band, as both its position and intensity can vary from one compound to another.

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The authors wish to thank W. H. Calkins, B. F. Day, R. H. Halliwell, R. C. Schreyer, I. D. Webb, and the other Du Pont chemists who made samples of many of the nitrile compounds available for this work. Thanks are due also to John Mitchell, Jr., and Donald Milton Smith for their assistance in the work and in the preparation of the manuscript, and to Richard C. Lord, Massachusetts Institute of Technology, and C. F. Hammer of this laboratory for their many helpful suggestions.

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(2) *Ibid.*, p. 131.
(3) Reitz, A. W., and Skrabel, R., *Ibid.*, 70, 398 (1937).

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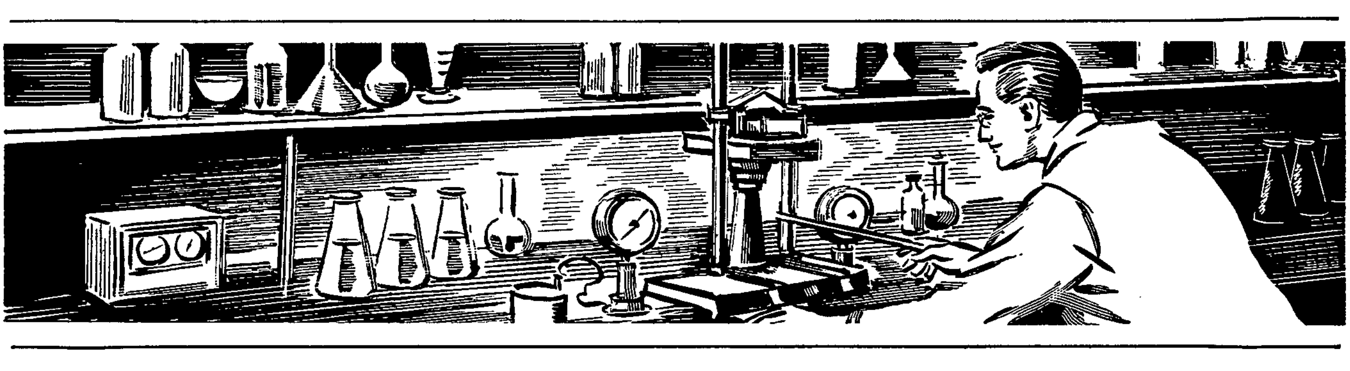

Theoretical Basis of the Bouguer-Beer Law of Radiation Absorption

FREDERICK C. STRONG[1], *Villanova College, Villanova, Pa.*

Presentations of the mathematical law governing the absorption of radiation as a function of the thickness and concentration of absorbing material are customarily based upon experimental observation. A complete derivation is presented, based only upon modern theories of matter and energy. Considering the radiant power of a beam as the number of photons passing per unit time and the process of absorption as the capture of photons by molecules or ions, the probability of capture is related to a ratio of areas in an element of material. This is then integrated over three dimensions for identical photons (monochromatic radiation) to yield the familiar absorption law. The general case of a beam with a continuous distribution of wave lengths is obtained by further integration and the result is given in several forms. In the belief that some of the equations are difficult to comprehend, graphical interpretations are presented, followed by analysis of possible methods of employing the law in practice. Finally, causes of apparent deviation are considered. Both the derivation and the graphical interpretations of the absorption law should make it more intelligible and fruitful for analysts.

THE author has observed that the relationship of absorption of radiation to thickness of absorbing material and concentration of an absorbing component is customarily presented as the result of experiment. For example, one reads that:

> As the initial radiant power varies, the fraction absorbed by a given sample of material remains constant.
>
> The rate of decrease of radiant power with thickness and with concentration is proportional to the initial power:

$$-\frac{dP_m}{dx} = a_1'P_m \tag{1}$$

$$-\frac{dP_m}{dc} = a_2'bP_m \tag{2}$$

where $\frac{dP_m}{dx}$ and $\frac{dP_m}{dc}$ are the rates of change of power of monochromatic radiation, P_m, with thickness and concentration, respectively, b is a fixed thickness, and a_1' and a_2' are positive constants. The usual presentation then continues with the integration of these equations, yielding

$$\frac{P_m}{P_{m,o}} = e^{-a'bc} \tag{3}$$

or related forms, $P_{m,o}$ being the initial radiant power. [Radiant power P, rather than intensity, I, has been recommended by the Committee on Letter Symbols of the American Physical Society (*5*) and by the Joint Committee on Nomenclature in Applied Spectroscopy, established by ASTM Committee E-2 on Emission Spectroscopy and the Society for Applied Spectroscopy.]

The author has often wished to see a derivation from theory only. Such a derivation can be carried out much more readily today, with the improved modern theories of matter and energy, than was possible in the times of Bouguer and Beer.

The exponential nature of the law suggests that probability plays a part. This has been recognized, but apparently never followed up by a published derivation. For example, Lange (*6*) stated in 1932 that the exponential dependence of radiation absorption by sols could be obtained by a consideration of probability. Fundamentally the process of absorption by colloidal particles and by molecules and ions would be identical.

DERIVATION FOR MONOCHROMATIC RADIATION

The quantum theory of radiation accounts for the phenomenon of absorption more readily than does the wave theory. According to the former, radiation consists of particles (quanta or photons) of energy $h\nu = hc/\lambda$, where h is Planck's constant, ν is the frequency of the radiation (when considered as a wave), c is its velocity, and λ is its wave length. Absorption is then to be interpreted as the capture of a photon by a molecule or portion of a molecule, thereby increasing its energy. Likewise, the radiant power is interpreted as the number of photons passing per unit time.

Consider a parallel radiation beam (Figure 1) in which the photons are identical (radiation is monochromatic) and the cross section of the beam is S.

Let the beam pass through a homogeneous absorbing medium with: (1) parallel faces perpendicular to the beam; (2) thickness b; (3) initial power of the beam entering the medium after reflection equal to $P_{m,o}$; and (4) power after traveling distance x equal to P_m.

Consider an element of absorbing material with cross section S and thickness dx (Figure 1). Passage of P_m through thickness dx will change it by dP_m. Because P_m decreases by absorption, dP_m is negative. Let dS_c be the projected area of regions in the element which will capture photons. It will be infinitesimal because the thickness is infinitesimal.

If a photon is passed perpendicularly through the element, the probability of its capture will be the ratio of capture area to total area, dS_c/S. If this is done at random a great many times (as would be the case for the photons in a beam), the count of the fraction captured would be $-\frac{dP_m}{P_m}$ and would be statistically equal to the probability of capture:

$$-\frac{dP_m}{P_m} = \frac{dS_c}{S} \tag{4}$$

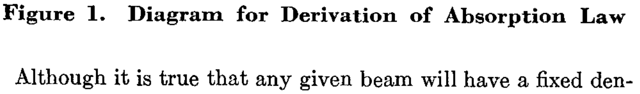

Figure 1. Diagram for Derivation of Absorption Law

Although it is true that any given beam will have a fixed density of radiation determined by the optical system and will, therefore, not correspond to random passage of photons, the probability of photon capture will be unaffected, as the material is assumed to be macroscopically homogeneous.

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The material will in general contain more than one absorbing substance, each contributing to the area, dS_c:

$$dS_c = a_1'dn_1 + a_2'dn_2 + \ldots\ldots \qquad (5)$$

where a_1' is the capture cross section of a unit quantity (molecule, mole, gram, etc.) of species 1, dn_1 the number of units of species 1 in the volume element Sdx, etc. Substituting and changing signs,

$$\frac{dP_m}{P_m} = -\frac{1}{S}(a_1'dn_1 + a_2'dn_2 + \ldots\ldots \qquad (6)$$

[As the question of whether a photon can be absorbed by a molecule depends upon whether the energy of the photon (hc/λ) is capable of raising the energy of the molecule to a permitted state, the a's will be functions of wave length.] Summing over the interval $0 \leq x \leq b$,

$$\int_{P_{m,o}}^{P_m} \frac{dP_m}{P_m} = -\frac{1}{S}\left[\int_0^{n_1} a_1'dn_1 + \int_0^{n_2} a_2'dn_2 + \ldots\ldots\right] \qquad (7)$$

or

$$\ln \frac{P_m}{P_{m,o}} = -\frac{a_1'n_1}{S} - \frac{a_2'n_2}{S} - \ldots\ldots \qquad (8)$$

Substituting the spectrophotometric quantities, transmittance ($T = \frac{P}{P_0}$), and absorbance ($A = -\log T$), and retaining the subscript m to denote the monochromatic case,

$$A_m = \frac{a_1dn_1}{S} + \frac{a_2dn_2}{S} + \ldots\ldots \qquad (9)$$

$$T_m = 10 - \frac{a_1n_1}{S} - \frac{a_2n_2}{S} - \ldots\ldots \qquad (10)$$

where

$$a_i = a_i' \log e \qquad (11)$$

$$= 0.4343\ a \qquad (12)$$

Equations 8, 9, and 10 may be considered as equivalent statements of the absorption law in its most fundamental form—namely, in terms of quantity of substance in the path of the beam. [According to a recent intensive study (*7*) of Beer's original paper (*1*), this concept of the basis of absorption was also that of Beer. However, he chose to express it in terms of length and compensated for the use of different concentrations by considering that he had in effect changed the length of path. In other words, he did not use concentration as an explicit variable, contrary to prevailing opinion.]

In the interests of practicality, both concentration and path length are introduced as follows:

The volume, V, of the path through the medium is bS.

Therefore:

$$\frac{1}{S} = \frac{b}{V} \qquad (13)$$

and

$$\frac{n_1}{S} = \frac{n_1b}{V} = bc_1 \qquad (14)$$

since $n_1/V = c_1$, the concentration of component 1.

Substituting,

$$\ln \frac{P_m}{P_{m,o}} = -a_1'bc_1 - a_2'bc_2 - \ldots\ldots \qquad (15)$$

$$\log \frac{P_m}{P_{m,o}} = -a_1bc_1 - a_2bc_2 - \ldots\ldots \qquad (16)$$

$$A_m = a_1bc_1 + a_2bc_2 + \ldots\ldots \qquad (17)$$

$$T_m = 10^{-a_1bc_1 - a_2bc_2 - \ldots\ldots} \qquad (18)$$

EXTENSION TO FINITE BAND WIDTH

The above equivalent expressions for the absorption law involve monochromatic radiation, a condition that may be approached in practice but probably never quite attained. Filter photometers pass a wide wave-length band and spectrophotometers a band whose narrowness is limited by the intensity of the source of radiation, the sensitivity of the detector, and the resolution of the optical system (Figure 2) (*4*). Even an isolated line has been shown to have width. Hence, it is desirable to obtain a form of the law which applies to a band of finite width.

In Figure 2, it is apparent that the radiant power of the band is the area under the distribution curve—that is, the definite integral:

$$P = \int_{\lambda_1}^{\lambda_2} y\,d\lambda \qquad (19)$$

where y is the vertical axis in the figure. (It is of course necessary to avoid integration over a path containing the points of discontinuity of curves a and b. However, this can be done by dividing the area vertically at these points and integrating over each portion separately.) The meaning of y can be readily ascertained, as the integral is the sum of an infinite number of infinitesimal areas, dP:

$$dP = y\,d\lambda \qquad (20)$$

$$y = \frac{dP}{d\lambda}\left(\text{more correctly, } \frac{\partial P}{\partial \lambda}\right) \qquad (21)$$

An equivalent mathematical notation for this derivative would be P_λ' and it is frequently so represented, though usually with the prime omitted.

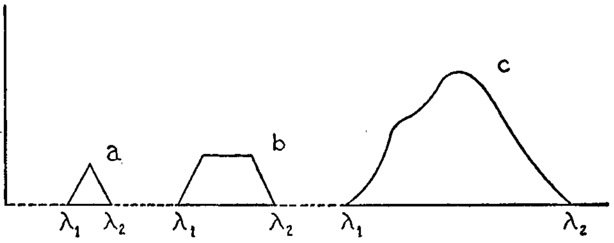

Figure 2. Wave-Length Distribution of Bands

- *a.* Exit slit of approximately same width as entrance slit
- *b.* Exit slit wider or narrower than entrance slit
- *c.* Filtered band

In order to apply the absorption law for monochromatic radiation to a finite band, an infinitesimal interval of the band can be considered. For band width $d\lambda$, the radiation is (*a*) essentially monochromatic and (*b*) of infinitesimal power, dP_o. If dP_o is reduced exponentially to dP by passage through a given solution,

$$T_m = \left(\frac{dP}{dP_o}\right)_{b,c_1,c_2,\ldots} = \frac{\partial P}{\partial P_o} = \frac{\partial P/\partial\lambda}{\partial P_o/\partial\lambda} = \frac{P\lambda}{P\lambda_{,o}} \qquad (22)$$

which provides an improved definition of T_m and a new statement of the absorption law for the monochromatic case:

$$P_\lambda = P_{\lambda,o}\,e^{-a_1'bc_1 - a_2'bc_2 - \ldots} \qquad (23)$$

To obtain the expression for finite band width,

$$dP = P_{\lambda,o}\,e^{-a_1'bc_1 - a_2'bc_2 - \ldots}\,d\lambda \qquad (24)$$

and

$$P = \int_{\lambda_1}^{\lambda_2} P_{\lambda,o}\,e^{-a_1bc_1 - a_2bc_2 \ldots}\,d\lambda \qquad (25)$$

This is the correct form of the absorption law for finite band width. In order to evaluate the integral mathematically, the variation of $P_{\lambda,o}$, a_1', a_2', etc., with λ must be known.

For application to analysis, the absorption law takes the form:

$$T = \frac{P}{P_o} = \frac{\int_{\lambda_1}^{\lambda_2} P_{\lambda,o}\, e^{-a_1'bc_1 - a_2'bc_2 - \cdots} d\lambda}{\int_{\lambda_1}^{\lambda_2} P_{\lambda,o}\, d\lambda} \tag{26}$$

However, it is more common to measure relative transmittance, $T_r = P/P_B$, where P_B is the radiant power transmitted by a blank containing all the substances present in the sample solution except the substance or substances being determined and all of the same thickness. If only one substance (component 1) is being determined, and if the solution is sufficiently dilute, or the absorptivities of the other components are sufficiently small that their absorbance in the sample solution is equivalent to the absorbance of the blank,

$$dP_B = P_{\lambda,o}\, e^{a_2'bc_2 - a_3'bc_3 - \cdots} d\lambda \tag{27}$$

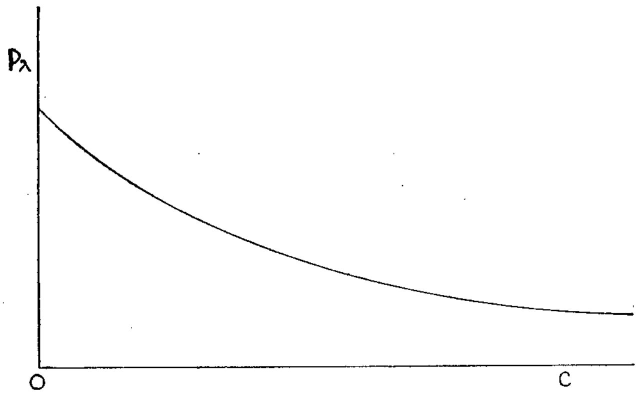

Figure 3. Curve of Equation $P_\lambda = P_{\lambda,o}10^{-abc}$

***b* constant**

Dividing Equation 24 by Equation 27,

$$T_{r,m} = \frac{\partial P}{\partial P_B}\, e^{-a_1'bc_1} \tag{28}$$

which is another form of the absorption equation for monochromatic radiation.

$$dP = \frac{\partial P_B}{\partial \lambda}\, e^{-a_1'bc_1}\, d\lambda \tag{29}$$

$$= P_{\lambda,B}\, e^{-a_1'bc_1} d\lambda \tag{30}$$

Integrating,

$$P = \int_{\lambda_1}^{\lambda_2} P_{\lambda,B}\, e^{-a_1'bc_1}\, d\lambda \tag{31}$$

Substituting,

$$T_r = \frac{P}{P_B} = \frac{\int_{\lambda_1}^{\lambda_2} P_{\lambda,B}\, e^{-a_1'bc_1}\, d\lambda}{\int_{\lambda_1}^{\lambda_2} P_{\lambda,B}\, d\lambda} \tag{32}$$

with

$$\int_{\lambda_1}^{\lambda_2} P_{\lambda,B}\, d\lambda = \int_{\lambda_1}^{\lambda_2} P_{\lambda,o}\, e^{-a_2'bc_2 - a_3'bc_3 - \cdots}\, d\lambda \tag{33}$$

GRAPHICAL INTERPRETATION OF ABSORPTION EQUATIONS

The meaning of the foregoing equations may not be readily grasped. Figures 3 to 6 will perhaps make them clearer. For simplicity, it is assumed that $a_2 = a_3 = \ldots\ldots\ldots = 0$, b is constant, and the subscript 1 is dropped from a_1 and c_1.

The exponential decrease of P_λ with concentration of one component for constant thickness is shown in Figure 3. For both concentration and wave-length variable, Figures 2, *c*, and 3 can be combined perpendicularly to give the three-dimensional graph of Figure 4.

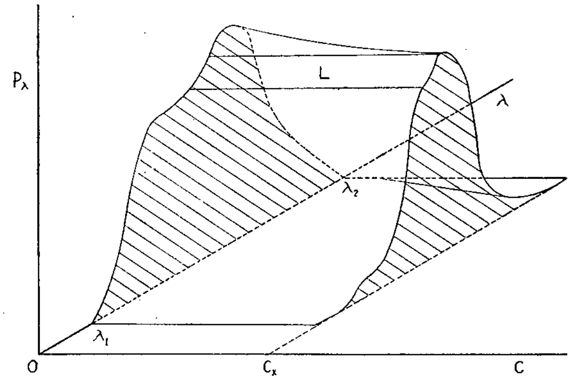

Figure 4. Surface of Equation $P_\lambda = P_{\lambda,o}10^{-abc}$

$a = f(\lambda)$ and *b* constant

The equation for $P_\lambda = f(c, \lambda)$ is that of a surface which intersects the P_λ, λ plane in the distribution curve for $P_{\lambda,o}$ with wave length and the parallel plane through $c = c_x$ in the curve for $P_\lambda = f(c_x, \lambda)$. The cross-hatched areas are, from left to right,

$$P_o \left(= \int_{\lambda_2}^{\lambda_1} P_{\lambda,o}\, d\lambda \right)$$

and

$$P \left(= \int_{\lambda_2}^{\lambda_1} P_\lambda\, d\lambda \right)$$

and their ratio is T. The portion of the surface marked L represents a region of the band spectrum not absorbed by the solution. The form of a graph for comparison with a blank—i.e., $P_\lambda = P_{\lambda,B}\, 10^{-abc}$—will be the same.

The three-dimensional graph of $T_m = 10^{-abc}$ is shown in Figure 5. The intersection of the surface with the T_m, λ plane will be a straight line at $T_m = 1$ because here $dP = dP_o$. The region L of Figure 4 becomes a horizontal rectangle. The areas corresponding to those evaluated in the previous figures no longer have significance, as T_m cannot be integrated directly to give T.

Figure 5 is transformed into Figure 6 by taking the negative logarithm of the vertical axis: $-\log T_m = abc$. The surface passes through the wave-length axis because for $c = 0$, $A_m = 0$. The plane in which $c = 1$ intersects the surface in a curve which is the variation of a with λ or the familiar absorption spectrum curve. Every plane perpendicular to the wave-length axis at some value λ_x will intersect the surface in a straight line with equation $A_m = a(\lambda_x)bc = kc$.

APPLICATION OF THE ABSORPTION LAW

Because the practical use of the absorption law in chemical analysis involves integration of unknown functions, any one of a number of procedures can be followed.

A. An experimental curve for the variation of absorbance with concentration can be determined, using a given band of fixed width and solutions of known concentrations. This curve can then be used for analyses under these conditions and with the same instrument. Even installation of a new radiation source might require revision of the curve.

B. The approximation that the absorptivities are constant in the wave-length interval can be made:

$$P = \int_{\lambda_1}^{\lambda_2} P_{\lambda,o}\, e^{-a_1'bc_1 - a_2'bc_2 - \cdots}\, d\lambda \tag{25}$$

$$\cong e^{-a_1'bc_1 - a_2'bc_2 - \cdots} \int_{\lambda_1}^{\lambda_2} P_{\lambda,o}\, d\lambda \tag{34}$$

$$\cong e^{-a_1'bc_1 - a_2'bc_2 - \cdots} \int_{0}^{P_o} dP_o \tag{35}$$

$$\cong P_o\, e^{-a_1'bc_1 - a_2'bc_2 - \cdots} \tag{36}$$

$$\text{or } T = \frac{P}{P_o} \cong e^{-a_1'bc_1 - a_2'bc_2 - \cdots} \tag{37}$$

Whether this approximation is sufficiently accurate can be determined experimentally by the procedure described in A, a straight line indicating that it is. It will be observed that the approximation consists of applying the equation for monochromatic radiation,

$$T_m = \frac{\partial P}{\partial P_o} = e^{-a_1'bc_1 - a_2'bc_2 - \cdots} \tag{23}$$

to finite band width.

When the sample solution is compared with a blank, the approximate equation becomes

$$T_r = e^{-a'bc} = 10^{-abc} \tag{38}$$

and

$$A_r = abc \tag{39}$$

where the subscript r denotes measurement relative to the blank.

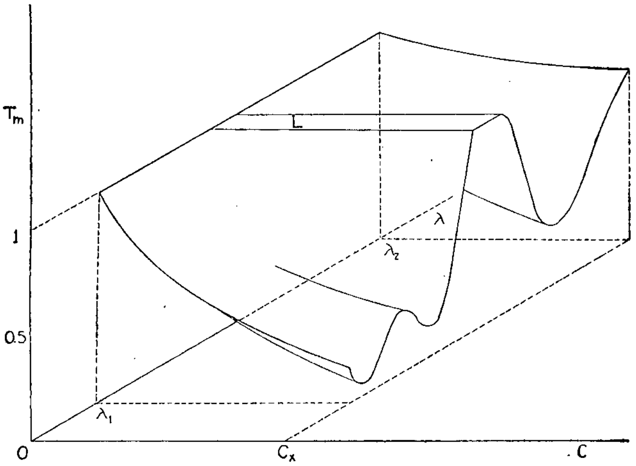

Figure 5. Surface of Equation $T_m = 10^{-abc}$

$a = f(\lambda)$ and b constant

The monochromatic equation will give the best results when (*a*) the pass band is as narrow as possible, (*b*) the band is centered on a wave length for which the absorptivity is a maximum or a minimum, and (*c*) the concentration range is kept small. Condition (*b*) is desirable for two reasons. Variation of absorptivity with wave length is small and the distribution of radiant power with wave length (when triangular) is at a maximum in the center of the band where variation of absorptivity with wave length is least.

C. Provided that the resulting curve is approximately linear and the instrument is suitable, transmittance or absorbance can be measured at varying band widths and extrapolated to zero band width.

D. Approximate functions can be substituted in the integrands of the expression for the relative transmittance and the value of the absorptivity at a given wave length calculated for known concentrations. This can then be used with any instrument for determining unknown concentrations, provided that the constants in the approximate functions are also determined for the instrument.

Eberhardt (*2*) has proposed approximate functions for spectrophotometry with the Beckman DU and similar instruments. Replacing a portion of his notation by that used in this paper, his function for $P_{\lambda,o}$ is:

$$P_{\lambda,o} = P_{\lambda_o,o}\left(1 + \frac{\lambda - \lambda_o}{\alpha\Delta\lambda}\right) \text{ for } \lambda_o - \alpha\lambda_1 \leq \lambda \leq \lambda_o \tag{40}$$

$$P_{\lambda,o} = P_{\lambda_o,o}\left(1 - \frac{\lambda - \lambda_o}{\beta\Delta\lambda}\right) \text{ for } \lambda_o \leq \lambda \leq \lambda_o + \beta\lambda_2 \tag{41}$$

The constants α and β correct for slight deviation from the triangular shape of $P_{\lambda,o}$ caused by nonlinear dispersion. $\lambda_o = {}^1/_2(\lambda_1 + \lambda_2)$ and $\Delta\lambda = {}^1/_2(\lambda_2 - \lambda_1)$.

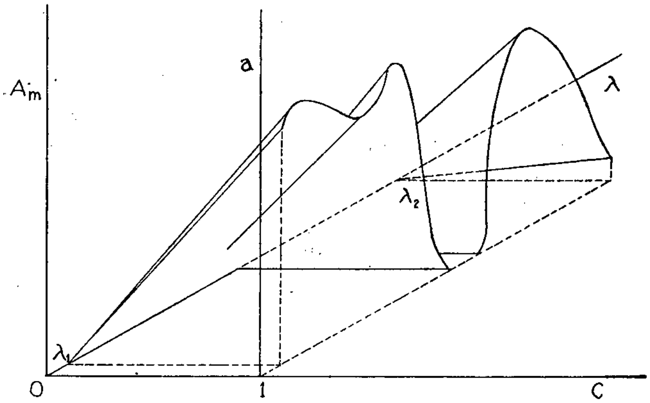

Figure 6. Surface of Equation $A_m = abc$

$a = f(\lambda)$ and b constant

For the exponential factor in the function for the blank he suggests

$$e^{-a_2'bc_2 - a_3'bc_3 - \cdots} \cong r(\lambda) = r(\lambda_o)[1 + \mu(\lambda - \lambda_o)] \tag{42}$$

where $r(\lambda_o)$ is a constant. This is satisfactory if absorption is not great and the band not too wide. For the absorptivity function he substitutes one of two alternative functions:

$$a_1'(\lambda) = a_1'(\lambda_o) + \gamma(\lambda - \lambda_o) + \delta(\lambda - \lambda_o)^2 \tag{43}$$

$$\text{or} \quad a_1'(\lambda) = a_1'(\lambda_o) - \gamma_1(\lambda - \lambda_o) \text{ for } \lambda_o - \alpha\Delta\lambda \leq \lambda \leq \lambda_o \tag{44}$$

$$a_1'(\lambda) = a_1'(\lambda_o) + \gamma_2(\lambda - \lambda_o) \text{ for } \lambda_o \leq \lambda \leq \lambda_o + \beta\Delta\lambda \tag{45}$$

These approximate functions are substituted in the equation for T_r (Equation 32) and integrated. Eberhardt gives equations for the two values of T_r corresponding to the function chosen for a_1' and also the simpler equations for cases where $\alpha = \beta = 1$ and $\mu = 0$.

Philpotts, Thain, and Smith (*8*) have proposed an error function as the approximation for $a_1'(\lambda)$ when a single absorption band in the infrared can be isolated:

$$a_1'(\lambda) \cong a_1'(\lambda_o)e^{-{}^1/_2\left(\frac{\lambda - \lambda_0}{l}\right)^2} \tag{46}$$

where l is a slightly different band width measurement (distance between points of inflection). The exponential is expanded and $e^{-a_1'(\lambda)bc}$ is again expanded. The integrals are evaluated by substituting five terms of the second expansion and assuming that $P_{\lambda,o}$ is constant over the interval. From the resulting equation, $a'(\lambda_o)$ is determined.

Hardy and Young (*3*) have inverted the integrals by means of a Fourier transformation and a Taylor expansion, obtaining an expression made up of a sum of derivatives. The treatment is very general, though mathematically complex, and deserves attention.

E. An attachment could perhaps be devised for a spectrophotometer which would automatically correct transmittance measurements to zero slit width. Hardy and Young have indicated how this ideal operation might be carried out electronically.

EXPERIMENTAL DEVIATIONS FROM THE ABSORPTION LAW

Upon examination, it is realized that few deviations from the absorption law observed experimentally are true deviations, as they result from nonfulfillment of the conditions of application of the law. A number of possible situations are enumerated below.

The phrase "...does not obey Beer's law..." commonly refers to the nonlinearity of the variation of absorbance with concentration. If the deviation is large, it usually indicates a mobile equilibrium that is shifted by dilution. Obviously, the deviation is not a failure of the law but of the experimenter in not including the absorption and correct concentrations of all components.

Nonlinearity in absorbance is to be expected for a pass band finite width. Here the "deviation" is present not in the measurement but in the approximate equation employed.

Scattering of a portion of the radiation represents a decrease in radiant power not caused by absorption, since some of it will not reach the detector. Fortunately, the relative error is usually small if absorption is significant.

Fluorescence and the Raman effect represent emission that can cause a positive error in the measurement of transmittance. These effects are also usually small in absorptiometry.

Absorptivities may change in concentrated solutions or at different temperatures, owing to changes in solvation. As this involves a change in the structure of the substance being determined, deviation is to be expected.

Change in absorptivity with temperature can be expected for another reason: The distribution of the energy states of the molecules would be changed, altering their average capture cross section for photons of given energy.

Photochemical decomposition of the sample may occur during irradiation, causing a change in concentration. The low intensity of pass bands of photoelectric instruments usually avoids this difficulty whenever it is theoretically possible.

At high values of radiant power, a saturation effect might be observed. With a relatively large number of molecules in a higher energy state due to absorption, the absorptivity would be altered. The obvious remedy for such a hypothetical situation would be to revert to low power radiation.

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PRECISION COLORIMETRY

General Method of Improving Precision in Multicomponent Spectrophotometry and Some Practical Consequences Thereof

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The principles of relative absorbance colorimetry have been extended to multicomponent systems. In order to achieve the highest possible precision in the concentration measurement, the analyst must work with absorptivity ratios which are in turn relatively determined. The principles of the method for obtaining these ratios and for conducting such analyses are developed herein. Application is made to a two-component system consisting of the permanganate and dichromate ions. A tenfold gain is obtained in the precision of the analytical results obtained by the relative method as compared with the results for this same system analyzed by the absolute method. Extension of this relative approach to multicomponent systems is outlined, as well as a general method for chemical analysis without sample weighing.

THIS paper presents a number of considerations dealing with the problem of analyzing multicomponent systems using spectrophotometric techniques. By a combination of a relative absorbance technique coupled with the use of absorptivity ratios precisely determined it is possible to reduce the error of measurement in cases such as these so as to make their spectrophotometric determination comparable in precision to those of volumetric or gravimetric techniques.

The principles of relative absorptiometry have been extensively treated in a group of papers dealing with the fundamental theory *(7-9)* as well as with a number of practical applications thereof *(2, 3, 5, 13)*. In all of these papers the emphasis has been on the determination of the unknown concentration of an absorber relative to that of a reference standard. Since such relative concentrations may be determined precisely, it follows that relative absorptivities may be determined with similar precision and, consequently, multicomponent systems possessing considerable overlap of their absorption bands may be analyzed with the same increase in precision available to systems already described in the literature.

Although some other workers have utilized relative absorptivity ratios in multicomponent analysis, the essential character-

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istic of their approach was to use two absolutely determined absorptivities rather than to make the relative measurement directly. The paper of Perry, Sutherland, and Hadden (*12*) should be examined for such an application to mixtures of xylenes and ethylbenzene possessing spectra in the ultraviolet region. Baroza (*1*) has utilized a similar approach to the analysis of successive chromatographic fractions. His treatment involved a comparison of an absorbance peak with the background absorbance.

Jones, Clark, and Harrow (*10*), using a simplified version of the principle outlined by Hardy and Young (*6*) coupled with relative absorbance measurements, have treated systems containing a number of dyes as well as other compounds. Their approach to the analysis of multicomponent systems requires a mechanical matching of the components and their respective concentrations. Once such a matching has been effected the relative transmittance function of the unknown and the matched standard will be identical not only at certain critical wave lengths but at all wave lengths. The method of spectrophotometric matching employed by these workers involved comparison of the unknown and a variable reference solution. This variable reference solution was prepared by adding controlled amounts of standardized solutions of the several components to a mixing compartment. The resulting solution was circulated between the mixing compartment and an absorption cell. Matching was effected by repeatedly measuring the relative transmittance as a function of wave length after addition of portions of the standardized solutions. Recently (*4*) there has come on the market a type of spectrocomparator which scans repeatedly a given spectral region at very high rates of speed and which can be made to plot a relative absorbance function on a cathode ray screen. Provision is also made to permit a mechanical assembling of the components in the solution in such a way that a spectral match may be effected.

The method treated in this paper is in principle nearly identical with that of Jones, Clark, and Harrow (*10*), but it is formulated for the analyst who may not possess a recording spectrophotometer and must therefore rely on a few measurements taken at discrete wave lengths. Since he will usually work at wave lengths where the components of interest have absorption maxima, his precision will be the best obtainable with the instrument in question and, although it is of interest from a qualitative point of view to plot total spectra, as was done by the above authors, no precision gain is achieved thereby. Furthermore, a saving of time is to be anticipated by the proposed method since there will not be a tedious hunting for the proper component concentrations as is necessary by the variable reference technique.

EQUATIONS FOR TWO-COMPONENT SYSTEMS

When two components are present in solution with absorption spectra which do not overlap, the concentration of each may be determined either by a relative or by an absolute measurement just as though they were separately in individual solutions. If their absorption spectra overlap, then compensation for this overlap must be made in the course of their simultaneous spectrophotometric determination.

An illustration of such a situation is represented in Figure 1. The two components, x and y, have absorption maxima at wave lengths, λ' and λ'', respectively. The heavy line represents the light absorption characteristics of the mixture; the two dotted lines give similar information for the two components if measured separately. The two spectra have purposely been selected as shown for the purpose of simplifying the mathematical argument on error. These spectra are symmetrical in character and of equal absorptivity. Unless specifically stated the argument below will be based upon this figure in spite of its general character. This is made necessary by the number of parameters involved.

At any particular wave length the absorbance of the mixture will be the sum of the two individual absorbances so that for λ' and λ'' the following expressions apply:

$$A' = A'_x + A'_y = a'_x c_x + a'_y c_y \qquad (1)$$

$$A'' = A''_x + A''_y = a''_x c_x + a''_y c_y \qquad (2)$$

In these equations a and c represent the absorptivity coefficients and the concentrations, respectively, of the two components. The path length of the light in the absorption cell is considered to be unity and therefore is not represented here. To obtain the values for the concentrations of x and y the two equations are solved simultaneously with the result shown in 3a and 3b:

$$c_x = \frac{\dfrac{A'}{a'_x} - \dfrac{A''}{a''_y} \times \dfrac{a'_y}{a'_x}}{1 - \dfrac{a'_y}{a'_x} \times \dfrac{a''_x}{a''_y}} \quad (3a); \qquad c_y = \frac{\dfrac{A''}{a''_y} - \dfrac{A'}{a'_x} \times \dfrac{a''_x}{a''_y}}{1 - \dfrac{a'_y}{a'_x} \times \dfrac{a''_x}{a''_y}} \quad (3b)$$

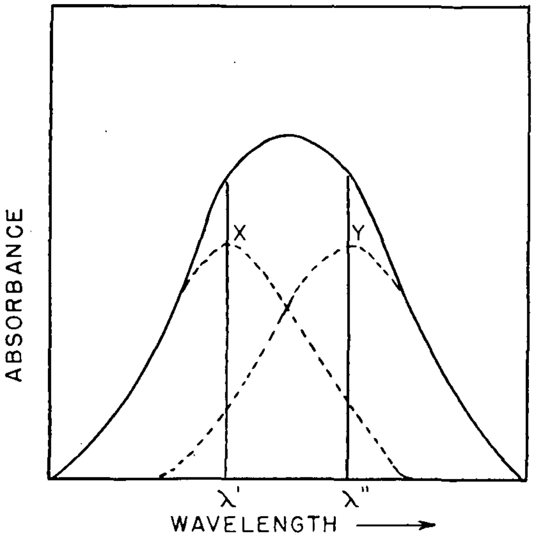

Figure 1. Two-Component System

Let us now consider in detail the solution given in Equation 3a to see the nature of the difficulties of obtaining high precision by this method. It is evident that if the quantities A' and A'' are determined by an absolute method, then the error of their measurement will be very much larger, possibly ten times more, than if they were measured by a relative method. Similar considerations also apply to the absorptivity coefficients involved since it can be demonstrated that the relative error of an absorptivity coefficient measurement is identical with that for a concentration measurement.

It is mathematically possible to derive an expression for the relative error of the c_x measurement, but the equation obtained is so complex that an examination of it is likely to be more confusing than helpful to the reader. The essential points, however, may be stated satisfactorily in a semiquantitative manner.

In the first place c_x is a quantity equal to the difference between the terms:

$$\frac{\dfrac{A'}{a'_x}}{1 - \dfrac{a'_y}{a'_x} \times \dfrac{a''_x}{a''_y}} \quad \text{and} \quad \frac{\dfrac{A''}{a''_y} \times \dfrac{a'_y}{a'_x}}{1 - \dfrac{a'_y}{a'_x} \times \dfrac{a''_x}{a''_y}}$$

When the overlap of the absorption bands is slight, the second term is trivial because a'_y/a''_y will be very small. The value of the numerator will approach A'/a'_x—i.e., c_x—while the value of the denominator will be nearly unity. The relative error of the concentration measurement will be $e \times \Delta(I/I_o)$ in the best case—i.e., when the transmittance is 36.8%. $\Delta(I/I_o)$ is the uncertainty of a transmittance measurement while e (= 2.72) is the napierian. On the other hand, if the overlap is so great that in a limiting situation the two absorption peaks occur at identical wavelengths, then the value of the numerator will be zero because A' and A'' will be equal while the ratio (a'_y/a''_y) will equal unity. The denominator will also be zero because a'_x and a''_x will be equal. The expression as a whole will be indeterminate; therefore, the error of measuring c_x in this case will be infinitely large. For intermediate cases of overlap the precision of analysis will also be intermediate. Consequently in absolute measurements the relative error will vary from the minimum value $e \times \Delta(I/I_o)$ when no overlap occurs to an infinitely large value when there is complete overlap.

With relative measurements the minimum relative error for the case with no overlap will be $\Delta(I/I_o)/A$ (7) (where A is the absorbance of the reference standard), while for complete overlap the relative error will also be infinitely large. Because the relative error is so much smaller in this method when there is little or no overlap, it is evident that this approach will be superior to the absolute method of measurement for all situations short of complete overlap in which the methods are equal, with infinite error. In practice this means that a tenfold gain may be anticipated with an instrument like the Beckman DU spectrophotometer in a relative measurement when the overlap is considerable but where the absorptivity ratios a''_x/a''_y and a'_y/a'_x are not much more than 0.5.

PRINCIPLE OF THE RELATIVE MEASUREMENT

In the relative method of measurement on a two-component system a reference standard of one component is compared against the unknown at the wave length of its absorption peak. A second reference standard of the other component is then compared with the unknown at the wave length of the absorption peak of this second component. The corresponding relations are:

$$a'_x c_x + a' c_y = a'_x c^s_x + \log (I_x/I_{\text{mix.}})' \qquad (4)$$

$$a''_x c_x + a \; c_y = a''_y c^s_y + \log (I_y/I_{\text{mix.}})'' \qquad (5)$$

In these expressions c^s_x and c^s_y represent the concentrations of the reference standards for component x and y, respectively. The log terms, $\log (I_x/I_{\text{mix.}})'$ and $\log (I_y/I_{\text{mix.}})''$, represent the difference in absorbance between a particular reference standard and the solution being analyzed. In general these log terms should be small in comparison with the reference absorbances used. Using a variable reference a perfect match may be effected between the unknown and standard absorbance. In this case the log term is zero and considerable simplification in the subsequent equations results.

Simultaneous solution of the two equations for c_x and c_y gives Equations 6 and 7.

$$c_x = \frac{c^s_x - \dfrac{a'_y}{a'_x} c^s_y + \dfrac{1}{a'_x} \log \left(\dfrac{I_x}{I_{\text{mix.}}}\right)' - \dfrac{a'_y}{a'_x \times a''_y} \log \left(\dfrac{I_y}{I_{\text{mix.}}}\right)''}{1 - \dfrac{a'_y}{a'_x} \times \dfrac{a''_x}{a''_y}} \qquad (6)$$

$$c_y = \frac{c^s_y - \dfrac{a''_x}{a''_y} c^s_x + \dfrac{1}{a''_y} \log \left(\dfrac{I_y}{I_{\text{mix.}}}\right)'' - \dfrac{a''_x}{a''_y \times a'_x} \log \left(\dfrac{I_x}{I_{\text{mix.}}}\right)'}{1 - \dfrac{a'_y}{a'_x} \times \dfrac{a''_x}{a''_y}} \qquad (7)$$

Although these equations appear formidable their complexity is more apparent than real because most of the terms are constants and once evaluated require no additional measurement. The denominators of both expressions are identical so that only one constant is needed for both.

If the ratios a'_y/a'_x and a''_x/a''_y are written as Y' and Y'', respectively, with $1/(1 - Y'Y'')$ being written as k then these two equations simplify to:

$$c_x = k \left[c^s_x + \frac{1}{a'_x} \log \left(\frac{I_x}{I_{\text{mix.}}}\right)' - Y' \left\{ c^s_y + \frac{1}{a''_y} \log \left(\frac{I_y}{I_{\text{mix.}}}\right)'' \right\} \right] \qquad (8)$$

$$c_y = k \left[c^s_y + \frac{1}{a''_y} \log \left(\frac{I_y}{I_{\text{mix.}}}\right) - Y'' \left\{ c^s_x + \frac{1}{a'_x} \log \left(\frac{I_x}{I_{\text{mix.}}}\right)' \right\} \right] \qquad (9)$$

Of the four terms in each expression the standard concentration terms will be the major ones, while the two log terms will be relatively small. If a perfect match were to be obtained between the two reference standards and the mixture these terms would become zero. In such a case these equations reduce to:

$$c_x = k[c^s_x - Y'c^s_y] \text{ and } c_y = k[c^s_y - Y''c^s_x]$$

To understand which of the terms are the principal ones affecting the precision of the concentration measurement consider the various parts of Equations 8 and 9 in turn in order to assess their effect on the final result. This treatment will be concerned with the maximum error possible rather than with any averaged values. Thus two uncertainties will always be treated as though they tend to reinforce each other.

Starting first with the constant term, k, it is seen that the uncertainty involved in this expression is determined by the sum of the uncertainties of Y' and Y'' as well as in the absolute value of the product $Y'Y''$. If it is assumed that the relative uncertainty of either of these ratios ($\Delta Y/Y$) is 0.001 (a value quite easy to obtain in practice) then the maximum uncertainty of the product is 0.002. Not until $Y'Y''$ is larger than 0.33 will the uncertainty of k equal 0.001. At lower values the uncertainty of this term will be substantially less or even trivial. When $Y'Y''$ has values equal to 0.2 and 0.1, $\Delta k/k$ will be 0.005 and 0.00022, respectively.

Since the average value of these absorptivity ratios have to be less than $(Y'Y'')^{1/2}$—i.e., $(0.33)^{1/2} \cong 0.57$—a requirement which is often easy to achieve in practice, it is apparent that the precision requirements for this term are not severe allowing a considerable overlap of the absorption curves.

The next two terms to be considered—i.e., the standard concentration terms—must be considered as a unit since it is the difference between them which is the important factor and not the value of the individual terms. The log terms are small between $(c^s_x - Y'c^s_y)$, which determines the magnitude of c_x, while it is the absolute uncertainties of c^s_x and $Y'c^s_y$ which determine the uncertainty of the difference. As this difference becomes small the relative error will increase and as the difference approaches zero it will become infinitely large. Therefore, this consideration requires that the highest possible absorbances be used so as to make the difference as large as possible for given values of Y' and Y''. Since the reference standards may be made with a precision of 1 part in 10,000, these terms are some of the most precise in the entire expression. The ratio Y', however, will introduce an error of about 0.001 c^s_y in the product of $Y'c^s_y$ since this 0.001 represents a reasonable error for an absorptivity ratio with the better spectrophotometers presently available. The effect of this uncertainty on c_x will be determined by the relative values of c^s_x and $Y'c^s_y$. When $Y'c^s_y$ is small with respect to c^s_x a larger error in Y' may be tolerated.

Finally, in spite of the fact that the two logarithmic terms are minor ones in most relative measurements, in this solution they constitute one of the major sources of error. The error introduced here will be determined by the ratio of uncertainty of the transmittance measurement, $\Delta(I/I_o)$, and the absorptivity coefficient of the particular reference component being used. Where I/I_o is close to unity the error will nearly equal $\Delta(I/I_o)/a$. It will exactly equal $\Delta(I/I_o)/a.I/I_o$ at all relative transmittance values.

The practical consequences of this discussion may now be summarized in the following rules:

Work at the highest possible absorbances in order to keep the difference $c^s_x - Y'c^s_y$ at a maximum.

Have the reference standards of such concentration values that the $\log I/I_{\text{mix.}}$ terms are very close to zero but certainly not larger than 0.2 or 0.3.

Make precise determinations of the absorptivity ratios.

MEASUREMENT OF ABSORPTIVITY RATIOS

Provided that no deviation from the absorption law occurs, the precise determination of an absorptivity ratio at any given wave length is effected by comparing a known concentration of one component against a known concentration of the other. Each of the components is placed in its own cuvette and then after the spectrophotometer is balanced at 100% transmittance for one, the other is substituted. For each component the absorption law relations would be:

$$\log \left(\frac{I_o}{I_x}\right)' = a'_x c_x$$

$$\log \left(\frac{I_o}{I_y}\right)' = a'_y c_y$$

If comparison of one is made against the other, then:

$$\log\left(\frac{I_x}{I_y}\right)' = a'_y c_y - a'_x c_x = a'_x c_x(\alpha Y' - 1) \qquad (10)$$

where $\alpha = \frac{c_y}{c_x}$ and $Y' = \frac{a'_y}{a'_x}$

By careful adjustment of the concentration of one of the components, $(I_x/I_y)'$ can be made to equal unity and then $a'_x c_x(\alpha Y' - 1)$ will equal zero. Since $a'_x c_x$ has a finite value, $(\alpha Y' - 1) = 0$ and $Y' = 1/\alpha = c_x/c_y$.

If the system corresponds to the absorption law, the value of the product of absorptivity ratio Y and the concentration ratio, α, will be known with increasing precision as the absorbance, $a_x c_x$, is given larger and larger values. For highest precision, therefore, the maximum absorbance which the instrument can handle should be used.

In practice it is not necessary to balance exactly one solution against the other. Instead a concentration of component y is taken which possesses a maximum absorbance at the wave length of the absorption peak for component x. The solution of this component is now compared with a range of concentration of component x. If a plot of ratio α versus $\log(I_x/I_y)'$ is made a straight line will be obtained. By interpolation it can then be ascertained what value of α will make the relative absorbance term zero. In order that the precision of y be determined solely by the instrumental error it is a necessary requirement that the errors in the concentration values be small with respect to the instrumental error.

The principal term in Equation 10 which determines the instrumental precision is the absolute value of $a'_y c_y$. The value of a'_y will usually be less than a'_x because the absorption maximum for component y is at λ″. The analyst is therefore obliged to work with the highest possible concentrations of y when determining the absorptivity ratio, and often solubility restrictions control the value of $a'_y c_y$. At λ″ where a''_x/a''_y is determined similar considerations apply to the other component and to the determination of this ratio.

In the measurement of absorptivity ratios by the procedure outlined there is the stated requirement that the absorption law must hold for each of the components at both of the wave lengths employed if the ratios are to be concentration independent. The analyst may not assume this to be true without experimental verification. There are several ways that this verification may be effected. The most obvious way is to measure the ratio at a number of absorbances covering the range of values which will ordinarily be used in practice. Since the slits are opened to compensate for increased absorbance in the reference standards, it is obvious that apparent deviations will be enhanced in any system at a higher absorbance and consequently variation of the ratio may be anticipated.

A second way to establish invariance of the absorptivity ratio is to make a measurement of the relationship between the concentration of any one reference standard at the two wave lengths to be employed as a function of the slit width ratio in this system. If it is found that the relationship $c = \frac{r}{a}\log\left(\frac{S_o}{S}\right)_\lambda$, as outlined previously (*9*), fits for all concentrations, then the probability of invariance of the ratio is high. In this expression c and a are the concentration and absorptivity coefficient of the reference absorber, r is a term which characterizes the slit function of the instrument having a value of 2.0 in the properly aligned Beckman DU spectrophotometer, S_o and S are the slit widths for the solvent and for the solution of concentration c, respectively.

Occasionally a situation will be encountered in which solubility limitations will make it impossible to measure the ratio at the highest possible absorbance that may be encountered in an analysis—for example, if component y should possess a limited solubility so that at wave length λ′ it may not be possible to obtain an absorbance large enough to test for variations of the ratio, one can proceed in the following way.

First, a nearly saturated solution of component y is prepared and its absorbance estimated absolutely at λ′. Then enough of component x is added to bring the absorbance at that wave length to any desired value. It is necessary, of course, that the concentrations of both these components be known precisely. Now this solution may be directly matched with the solution containing only component x. The equality of absorbances in the two cuvettes will be as follows:

$$A_y + A_x = A_x^* \text{ and, therefore, } Y' = \frac{c_x^* - c_x}{c_y}$$

In this way it will be possible to see whether Y' deviates at the highest possible absorbance. Such a method of measurement at the highest absorbance will not result in any improvement in the precision of the y' determination but will only provide a test of its invariance.

In the case of an absorption law deviation the ratio may increase or decrease as the absorbance is raised. When this occurs resort must be made to a plot of Y' and Y'' as functions of the standard concentrations of x and y, respectively. During the course of the analysis then, when a reference standard concentration is known for the system under analysis, the analyst simply consults the above plot and inserts the proper coefficients into Equations 8 and 9. Where the deviations of a given system are pronounced the considerations outlined in (*9*) concerning the maximum apparent absorbances to be used must be kept in mind.

SYSTEMS OF MORE THAN TWO COMPONENTS

For a system containing three absorbers, x, y, and z, whose maxima are at λ′, λ″, and λ‴, the following relations would apply:

$$a'_x c_x + a'_y c_y + a'_z c_z = a'_x c_x^* + \log\left(\frac{I_x}{I_{\text{mix.}}}\right)'$$

$$a''_x c_x + a''_y c_y + a''_z c_z = a''_y c_y^* + \log\left(\frac{I_y}{I_{\text{mix.}}}\right)''$$

$$a'''_x c_x + a'''_y c_y + a'''_z c_z = a'''_z c_z^* + \log\left(\frac{I_z}{I_{\text{mix.}}}\right)'''$$

Six absorptivity ratios are needed since at each wave length two must be determined. There is no difficulty in formulating the equations for any number of components. On the other hand, for n components n equations are needed and $n(n - 1)$ absorptivity ratios must be determined. The solution of these equations becomes laborious and beyond the three-component system would be unprofitable unless a mechanical computer for such equations is available.

If a neutral wedge whose absorbance calibration was known precisely at the wave lengths employed were used, so that the $\log(I/I_{\text{mix.}})$ terms could all be made zero, then considerable simplification of the final equations results. Since neither of these aids were available to the authors more complex systems were not studied experimentally.

For the analyst operating in a well-equipped instrumental laboratory, the higher component systems may be treated with very little additional increase in error. There is, in fact, the interesting possibility of performing quantitative analyses without weighing the individual samples on the analytical balance. The way this can be performed will now be outlined.

COLORIMETRIC WEIGHING OF SAMPLES

Colorimetric analyses may be performed without weighing a sample on a chemical balance, providing the system meets either of the following sets of requirements without having extensive overlap of the absorption bands.

1. If n components of the sample effectively represent better than 99.5% of the total sample, the percentages of the n components may be established simply by knowing $n - 1$ concentration ratios.
2. If the sample is essentially a pure one with only trace concentrations of impurities to be determined, then the main element

may be used to give the sample weight and thus allow the establishing of the trace percentages.

These sets of requirements will be illustrated by considering a number of simple examples:

Suppose that a given sample is almost pure but has small traces of some impurity in it. Let us call the main substance component x, and the impurity, component y. Now, if one takes an unweighed sample, unweighed in a gravimetric sense, and measures the absorbance due to component x, then the size of the sample taken will be known. Therefore, the determination of the impurity, y, may be performed in the usual way and the percentage of that impurity may now be computed. This is the simplest possible case that we might consider.

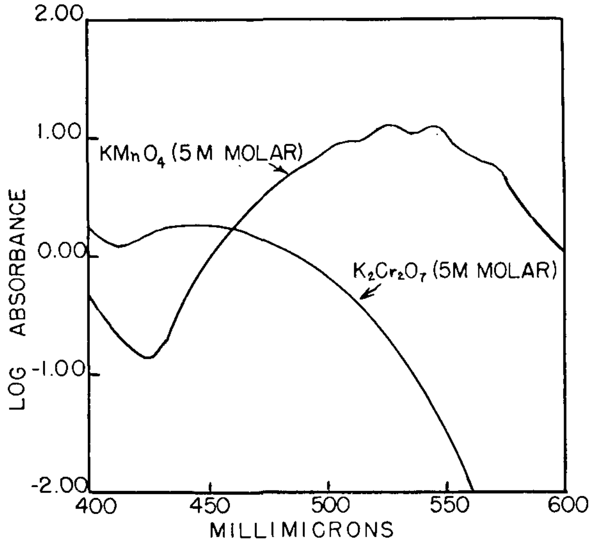

Figure 2. Spectra of Dichromate and Permanganate in 1 *M* Sulfuric Acid

Obviously, if there were two or more impurities it might be possible to determine them in this same sample providing suitable absorption spectra can be found, but the essential requirement of this approach is that the main component x represents effectively 99.5% or better of the total sample if the weighing error is to be less than 0.5%.

Another illustration involves x and y both as major components, as they well might be in an alloy or in some solution undergoing distillation. If the sample contains only these two components, then when the ratio of one to the other is known the percentage composition is also known. If x plus y equals effectively 100% of the sample and the ratio of $x/y = R$ as determined, then the percentage of A will equal a hundred times $R/R + 1$, while the percentage of B will equal $100/R + 1$.

In a three-component case—that is, where $x + y + z$ effectively represent the total sample—at least two concentration ratios must be determined in order to solve for the percentage distribution of the three components. There are a number of situations in plant control, in fractionation experiments, and in the measurement of concentration changes with time, temperature, or some other parameter where analysis of this sort is useful and the taking of a sample weight undesirable. These comments are made here with the object of drawing attention to such possibilities latent in multicomponent analysis.

EXPERIMENTAL

To test the propositions outlined above, measurements were performed on a two-component system consisting of permanganate and dichromate ions dissolved in 1 *M* sulfuric acid solution. For this system measurements were made by a relative and by an absolute technique in order to permit a comparison of the precision of the two approaches.

Standard solutions of potassium permanganate and of potassium dichromate were prepared according to the usual analytical procedures. Individual portions of these solutions were appropriately diluted and their absorption spectra determined on a Beckman DU spectrophotometer using a 1-cm. absorption cell. These solutions were all 1 *M* with respect to sulfuric acid. In Figure 2 a plot of log A versus wave length is given for these two substances. It is seen on examination of this plot that the peak for the dichromate solution is at about 450 mμ where the absorptivity coefficient of the permanganate ion is about half that of the dichromate. In the region of the permanganate absorption peaks, the absorptivity coefficient for the dichromate is relatively small so that only at the 450-mμ wave length is the overlap sufficient for a comparative test of the relative and absolute methods. On the other hand, previous studies had indicated that both of these components could be analyzed precisely by spectrophotometric methods and consequently difficulties of chemical instability, absorption law deviations, and so on were not to be anticipated for this system. It was used, therefore, in spite of the absence of overlap in the 546-mμ region.

Table I. Absorptivity Ratio

(Solutions are 1 molar with respect to H_2SO_4. 1-cm. matched cells used. Mazda light source. Solutions compared at maximum sensitivity.)

$K_2Cr_2O_7$ and $KMnO_4$ Solutions at 450 Mμ

Concn. $KMnO_4$, Millimoles	Concn. $K_2Cr_2O_7$, Millimoles	Absorbance	$\frac{a_{KMnO_4}}{a_{K_2Cr_2O_7}}$	Slit Width, Mm.
5.018	2.500	0.936	0.4853	0.202
5.098	2.500	0.936	0.4866	0.201
2.360	1.000	0.371	0.4864	0.107
2.360	1.000	0.371	0.4853	0.108
0.9770	0.5000	0.185	0.4857	0.058
			Av. 0.4859	± 0.0005

$K_2Cr_2O_7$ and $KMnO_4$ Solutions at 546 Mμ

Concn. $K_2Cr_2O_7$, Millimoles	Concn. $KMnO_4$, Millimole	Absorbance	$\frac{a_{K_2Cr_2O_7}}{a_{KMnO_4}}$	Slit Width, Mm.
97.70	0.2525	0.585	0.00356	0.042
48.85	0.1504	0.350	0.00328	0.066
48.85	0.1133	0.263	0.00347	0.060
48.85	0.1133	0.263	0.00337	0.040
			Av. 0.00342	± 0.00009

A measurement of the absorptivitity ratios by the relative method was made and the data obtained are listed in Table I.

Table I shows that at 450 mμ $\frac{a_{KMnO_4}}{a_{K_2Cr_2O_7}}$ has a value of 0.4859 ± 0.0005, while absolute measurements not tabulated here give that ratio a value of 0.487 ± 0.005. Thus, in this instance the precision of the ratio determined relatively is about ten times more precise than the value determined as the ratio of two absolute measurements. For $\frac{a_{K_2Cr_2O_7}}{a_{KMnO_4}}$ the value determined relatively is 3.42×10^{-3} with an uncertainty of $\pm 0.09 \times 10^{-3}$, whereas on an absolute basis the value obtained was $3.70 \pm 0.21 \times 10^{-3}$. Because the ratio is so small the precision of the ratio measurement was only slightly better than in the absolute case.

A number of synthetic mixtures were next prepared in which the relative concentrations of the dichromate and permanganate were varied one hundredfold and these solutions were analyzed by absolute and by relative methods. The equations used in the absolute case were as follows:

$$\text{Millimoles } K_2Cr_2O_7 = 2.70\ A_{450} - 0.21\ A_{546}$$

$$\text{Millimoles } KMnO_4 = 0.430\ A_{546} - 0.010\ A_{450}$$

The corresponding equations for the relative case are as follows:

$$c_{Cr} = 1.0017 \times \left[c^{s}_{Cr} - 0.4859c^{s}_{MnO_4} - 2.70 \log\left(\frac{I_{mix.}}{I_{Cr}}\right)_{450} + 0.210 \log\left(\frac{I_{mix.}}{I_{Mn}}\right)_{546}\right]$$

$$c_{Mn} = 1.0017 \times \left[c^{s}_{Mn} - 0.00342c^{s}_{Cr} - 0.430 \log\left(\frac{I_{mix.}}{I_{Mn}}\right)_{546} + 0.0086 \log\left(\frac{I_{mix.}}{I_{Cr}}\right)_{450}\right]$$

The concentrations in these equations are in millimoles. The subscript "mix." refers to the mixtures. The results of these analyses are given in Table II.

Table II shows that the relative method is 10 to 12 times more precise than the absolute method in this particular example.

Deviations of 1 to 2 parts per 1000 obtained for both the dichromate and permanganate determinations demonstrate again that the relative absorbance method is at least as good as standard volumetric and gravimetric methods for the analysis of these components.

Analyses of several National Bureau of Standards steels were made in order to test the relative absorbance method with actual samples. These steels contained varying amounts of chromium and manganese. The samples were prepared by dissolution in sulfuric and nitric acids, treatment with persulfate and periodate to develop stable dichromate and permanganate colors, and addition of phosphoric acid to complex iron and prevent interference at 450 mμ. The use of persulfate and periodate for the simultaneous determination of chromium and manganese was described by Lingane and Collat (*11*).

The actual procedure was as follows:

An appropriate sample (0.5 to 2 grams) of the steel was placed in a 400-ml. beaker provided with a cover glass. Fifty milliliters of distilled water and 12 ml. of sulfuric acid were added. (This quantity of acid will result in a final solution that is 1 molar with respect to sulfuric acid.) The solution was boiled until the reaction subsided, then it was cooled and 5 ml. of nitric acid were cautiously added. The solution was boiled until fumes of sulfuric acid were observed and then diluted to approximately 75 ml. and heated to dissolve precipitated salts. Next it was filtered. The filter paper was thoroughly washed. To the filtrate 3 to 5 grams of potassium persulfate and a few small crystals of silver nitrate were added, after which it was heated to boiling and boiled for 7 minutes to destroy the excess persulfate. Next 15 ml. of phosphoric acid and 1 gram of potassium periodate were added, followed again by heating and boiling for 5 minutes. When cool the solution was transferred to a 250-ml. volumetric flask and there diluted with distilled water to volume.

Table II. Analysis of Synthetic Mixtures

(Comparison of relative and absolute colorimetry)

Soln. No.	Ratio, $K_2Cr_2O_7$/$KMnO_4$	Relative Method: Millimoles of $K_2Cr_2O_7$, Added	Relative Method: Millimoles of $K_2Cr_2O_7$, Calcd.	Relative Method: % diff.	Absolute Method: Millimoles of $K_2Cr_2O_7$, Added	Absolute Method: Millimoles of $K_2Cr_2O_7$, Calcd.	Absolute Method: % diff.
1	1/1	0.9770	0.9780	0.10	0.9770	1.005	2.9
2	2/1	1.954	1.952	0.10	0.4885	0.4879	0.12
3	5/1	2.950	2.942	0.27	1.250	1.268	1.4
4	10/1	4.495	4.496	0.02	1.250	1.265	1.2
5	20/1	4.885	4.894	0.18	2.500	2.522	0.88
6	50/1	4.885	4.890	0.10	4.885	4.794	1.9
7	100/1	4.885	4.886	0.02	4.885	4.818	1.4
		Av. % diff. =		0.11	Av. % diff. =		1.4

Soln. No.	Ratio, $K_2Cr_2O_7$/$KMnO_4$	Relative Method: Millimoles of $KMnO_4$, Added	Relative Method: Millimoles of $KMnO_4$, Calcd.	Relative Method: % diff.	Absolute Method: Millimoles of $KMnO_4$, Added	Absolute Method: Millimoles of $KMnO_4$, Calcd.	Absolute Method: % diff.
1	1/1	0.9770	0.9784	0.14	0.9770	0.9213	5.7
2	2/1	0.9770	0.9794	0.25	0.2360	0.2365	0.21
3	5/1	0.5900	0.5896	0.07	0.2360	0.2363	0.13
4	10/1	0.4496	0.4499	0.07	0.1221	0.1204	1.4
5	20/1	0.2443	0.2446	0.12	0.1221	0.1202	1.6
6	50/1	0.0977	0.0978	0.10	0.0977	0.0964	1.3
7	100/1	0.0489	0.0491	0.41	0.0489	0.0478	2.2
		Av. % diff. =		0.17	Av. % diff. =		1.8

Table III. Analysis of Bureau of Standards Steels

(Comparison of relative and absolute colorimetric methods)

(Mazda light source; 1.002-cm. Corex cells; sensitivity knob three turns from least sensitive position)

Sample No.	NBS Value, % Cr	Relative Method: % Cr found	Relative Method: % diff.	Relative Method: Soln. A_{450}, mμ	Absolute Method: % Cr found	Absolute Method: % diff.	Absolute Method: Soln. A_{450}, mμ
72c	0.967	0.974	0.72	0.2867	1.008	4.2	0.2867
72d	1.03	1.04	0.97	0.3372	1.05	1.9	0.3372
36A	2.41	2.42	0.41	0.7696	2.46	2.1	0.3863
135	5.15	5.20	0.97	1.420	5.26	2.1	0.4103
133	13.59	13.70	0.81	1.658	13.91	2.4	0.5645
73a	14.09	14.16	0.50	1.699	13.76	2.3	1.699
	Av. % diff.		0.73			2.5	

Sample No.	NBS Value, % Mn	Relative Method: % Mn found	Relative Method: % diff.	Relative Method: Soln. A_{546}, mμ	Absolute Method: % Mn found	Absolute Method: % diff.	Absolute Method: Soln. A_{546}, mμ
72c	0.539	0.537	0.37	1.222	0.530	1.7	1.222
72d	0.537	0.537	0.00	1.357	0.517	3.7	1.357
36A	0.432	0.438	1.4	1.377	0.430	0.46	0.6990
135	0.458	0.460	0.44	1.398	0.440	3.9	0.3893
133	0.799	0.798	0.13	1.155	0.788	1.4	0.3768
73a	0.249	0.252	1.2	0.4067	0.243	2.4	0.4067
	Av. % diff.		0.59			2.3	

Table IV. Bureau of Standards Steels, NBS Certificate Values

72c, Cr-Mo steel	Mn 0.539 Si 0.286 Mo 0.216	Cr 0.967 Cu 0.098 C 0.329	P 0.015 Ni 0.113	S 0.018
72d, Cr-Mo steel	Mn 0.537 Si 0.276 Mo 0.210	Cr 1.03 Cu 0.041 C 0.310	P 0.017 Ni 0.125	S 0.011 V 0.005
36A, Cr-Mo steel	Mn 0.432 Si 0.356 Mo 0.920	Cr 2.41 Cu 0.114 Sn 0.011	P 0.014 Ni 0.243 C 0.120	S 0.017 V 0.006
135 Cr-Mo steel	Mn 0.458 Si 0.383 Mo 0.575	Cr 5.15 Cu 0.076 C 0.094	P 0.017 Ni 0.083	S 0.010 V 0.010
133 Cr-Mo steel	Mn 0.799 Si 0.433 Mo 0.559	Cr 13.59 Cu 0.061 N 0.046	P 0.022 Ni 0.286 C 0.118	S 0.355 V 0.020
73a, stainless steel—14% chromium	Mn 0.249 P 0.015 Mo 0.069	Cr 14.09 Cu 0.080 W 0.091	S 0.031 Ni 0.159 N 0.036	Si 0.311 V 0.028 C 0.349

Table III compares results of analyses of six National Bureau of Standards standard steels. The ratios of chromium to manganese in these steels are from 2 to 1 to 30 to 1. The results show the greater precision attainable with the relative absorbance method. Average deviations from the National Bureau of Standards certificate value of 7 and 6 parts per 1000 were obtained for chromium and manganese, respectively, using the relative absorbance method. Average deviations of 24 parts per 1000 were obtained using the absolute method.

The constituents of the steel samples are listed in Table IV, which shows that nickel, copper, and vanadium are present in variable amounts in these samples and, therefore, may require suitable correction in the reference standards if the highest possible precision is to be obtained.

ACKNOWLEDGMENT

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Thermistors for Cryoscopy of Air-Sensitive Materials

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A need arose for measuring the purity of samples of pentaborane by a simple method. By using a thermistor as the temperature-sensitive element for cryoscopy a very simple device was constructed that requires little attention or manipulation. It can be used to measure the purity of compounds by their freezing points with a precision of ±0.004°C. Provisions have been made to prevent contact of air with the sample. Because of its simplicity and ease of operation, the apparatus may be useful for other purity determinations.

IN ORDER to determine the purity of samples of pentaborane by the depression of the freezing point, a device was required that would incorporate methods of handling the sample entirely within a vacuum system, use relatively small (2-ml.) samples, utilize simple equipment, and be very easy to operate. In addition, it was desired that the method be capable of measuring purity to about 0.01 mole % (±0.01° C.). The device that was developed to meet these requirements may be useful for other purity determinations. Its useful range of temperature is from about +25° to −60° C., but this range may be extended in either direction by simple modifications.

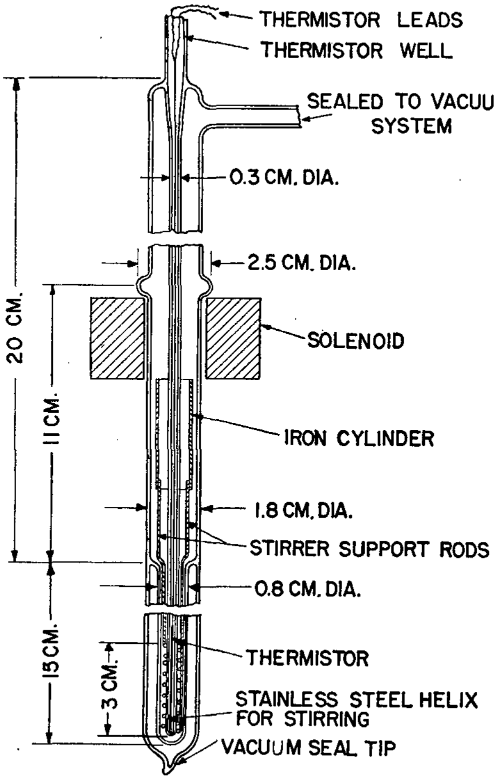

Figure 1. Freezing Point Cell

The required simplicity in the temperature-measuring circuit was achieved by using a thermistor as the temperature-sensitive element (*7*). The characteristics of thermistors that make them particularly useful for this application may be illustrated by comparing them with the more familiar platinum resistance thermometers, which have been used extensively in cryoscopy (*3*).

Thermistors (*5*) have a 4% change in resistance per degree change in temperature, as compared with 0.4% per degree for platinum, so that the relative change in resistance is ten times as great for small increments of temperature. The specific resistance of a typical thermistor material is 10^9 times as great as that of platinum at 0° C. Thermistors for temperature measurements can be made of these materials with a wide range of characteristics, but the particular thermistor used in this application (Type 14B, manufactured by Western Electric Co.) has a resistance of 2500 ohms at 20° C. as compared with 25 ohms for a platinum resistance thermometer. With such a high resistance, problems of lead resistance, contact resistance, etc., do not occur. Resistances in the range of several thousand ohms can be accurately compared on very simple, rugged, and inexpensive apparatus.

The temperature-sensitive portion of a thermistor is a bead, a fraction of a millimeter in diameter. In the type used, this bead is enveloped in one end of a glass tube 0.1 inch (0.25 cm.) in diameter and 3 inches long, with the leads opposed to the bead. Other kinds of thermistors are available (*1*).

FREEZING POINT CELL

The freezing point cell used is slightly modified from one used by Newkirk (*4*). Details of its construction are shown in Figure 1. The evacuated jacket is left unsilvered to permit energy transfer by radiation. The rate of energy transfer can be controlled by using various freezing mixtures. The sample is stirred by the stainless steel helix, which is attached to the iron cylinder by two heavy wires. A shoulder on the cell rests on a solenoid. This solenoid is activated about 120 times a minute by the current passed through a Microswitch each time it is closed by a double cam attached to the shaft of a 60 r.p.m. motor. This lifts the iron cylinder and the attached stirring helix about 1.5 cm. When the contact is broken the stirrer drops to its normal position.

FILLING THE CELL

The cell, which is sealed to a vacuum system, is filled by a vacuum distillation. In the case of pentaborane, the samples are cuts from a fractional distillation, and this method of filling is permissible. If the samples contain nonvolatile impurities, other

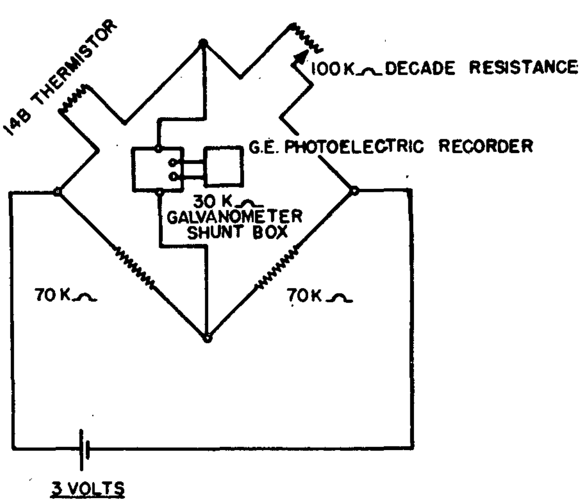

Figure 2. Circuit for Measuring Temperature with Thermistor

means of filling must be devised (*2*). In order to fill the cell completely, it must be immersed deeply enough to be cooled above the ring seal of the vacuum jacket, because the rate of heat transfer through the vacuum jacket is so slow. When all the sample has been condensed above the ring seal, the cell is closed off from the rest of the system, the refrigerant is lowered a bit, and the sample melts and runs down to fill the cell to a depth of about 5 cm., which is just sufficient to cover the top of the stirring helix at the top of its stroke. The volume of sample required is about 2.0 ± 0.2 ml. With the cell filled by this method, the cooling is continued at a rate of about 1° C. per minute until the sample is frozen while the freezing point is determined. The sample may be removed by another distillation. This is most easily accomplished by heating the sample with an infrared lamp after the refrigerant is removed.

Instead of being sealed directly to the vacuum system, the cell may be fitted with a stopcock and standard-taper joints for attaching it to the system. For materials that may be handled in air, the cell is made detachable, with a large tapered joint in the body of the cell above the shoulder, but without a side arm.

TEMPERATURE MEASUREMENT

The circuit used for measuring the resistance of the thermistor is shown in Figure 2. The components were chosen to operate satisfactorily at about the melting point of pentaborane, but can be used to −60° C., below which the resistance becomes too high to operate the recorder with adequate sensitivity, and to +25°, above which the resistance is too low to give satisfactory results with high resistances in other portions of the circuit. In order to operate at higher temperatures (to about +150°) the simplest change is to use a 14A thermistor, but lowering the other resistances in the circuit would also extend the range to higher temperatures.

To work at temperatures below −60° C. more drastic changes in instrumentation are required, the simplest being a more sensitive galvanometer, which will extend the range somewhat. By using a parallel impedance bridge (*6*) very high values of resistance can be measured accurately, but the extreme simplicity of the device is sacrificed.

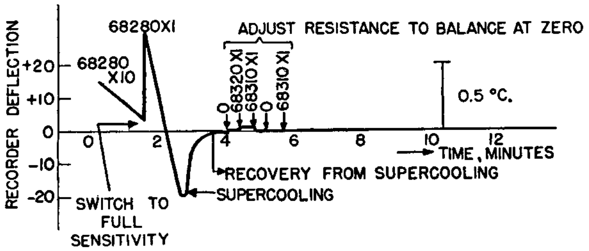

Figure 3. Typical Record of Freezing Point Determination

Chlorobenzene distillation cut 6. Freezing point found at 68,310 ohms. Freezing point of pure chlorobenzene was 68,280 ohms

A recorder is used rather than an indicating galvanometer, because it simplifies the gathering of data. The most convenient procedure for measuring the freezing point has been found to be as follows:

> The decade box is set to the resistance corresponding to the freezing point of the pure material. As soon as the cell is filled and the stirrer turned on, the recording is started, with the galvanometer shunt at low sensitivity. As the sample cools the sensitivity is increased as required. Generally the freezing point of the sample is exceeded, because of supercooling, but in a minute or two the freezing starts spontaneously and the resistance levels off to a very nearly constant value. [Fortunately, supercooling was not a problem with these particular samples, but it may be allowed for by the method described by Glasgow, Streiff, and Rossini (*3*) when necessary.] Then the resistance of the decade box is increased sufficiently to balance again at the zero of the recorder or galvanometer. The resistance so obtained is taken as a measure of the freezing point and its deviation from the freezing point of the pure material is a measure of the purity of the sample (*3*).

Figure 3 shows the kind of record obtained. Alternatively, the deviation of the recorder from zero at the freezing point is a measure of the purity.

By adhering closely to the procedure outlined above, heat leaks, variable temperature gradients, radiation errors, resistive heating of the thermistor element, heating by the stirrer, and other similar possible sources of error are compensated.

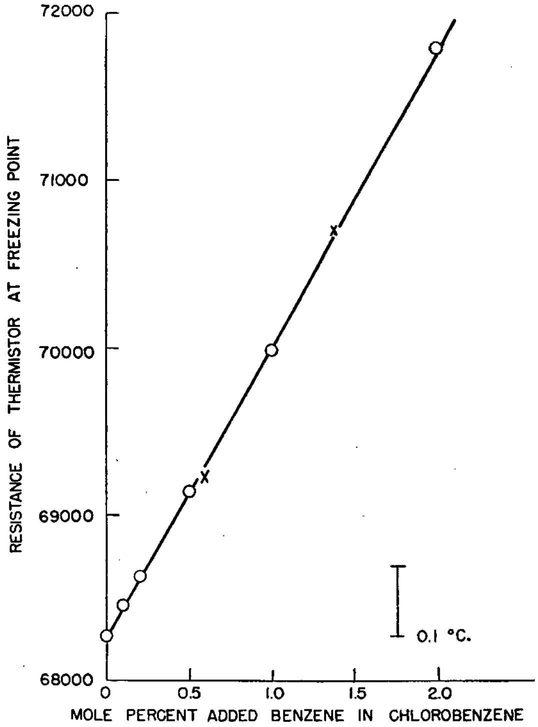

Figure 4. Calibration Curve for Impurities in Chlorobenzene

The measurements of the freezing point of an impure compound should be referred to the observed resistance for the freezing point for the pure material, and the resistance for known amounts of added impurities, rather than to an absolute temperature calibration.

The calibration of several thermistors has not changed by any measurable amount in several months. Zeffert and Hormats (*7*) also report satisfactory stability. However, until the stability is verified by a great deal more experience, occasional checks are recommended.

CALIBRATION AND PERFORMANCE

Chlorobenzene, melting point −45.3° C., and solutions of benzene in chlorobenzene were used to become acquainted with the behavior of the device. The freezing points on a series of samples, shown in Figure 4, are illustrative of the kind of data that can be obtained with the apparatus.

The time required to complete a determination, including filling and emptying the cell by vacuum distillations, is 2 hours or less, the actual determination requiring about 0.5 hour. The only manipulation of the measuring device is adjustment of the sensitivity of the shunt as the sample cools and a single balancing of the resistance on the decade box immediately after freezing starts.

The temperature of freezing can be determined with a precision of about ±0.004° C., using the simple components described here. A more sensitive indicating device would probably determine the freezing temperature more precisely, but the author has no data that would tell how reliable the results might be, since the various possible sources of error mentioned above might have an appreciable effect on the value obtained. At the limit of precision in the apparatus described (±0.004° C.) they do not seem to affect the results.

As the device was intended to check the purity of samples of a single compound, the calibration procedure is determination of the resistance corresponding to the freezing points of synthetic mixtures of the material under investigation. In the case of chlorobenzene, for example, the data obtained (Figure 4) are used in the form of a calibration curve; the purity of unknown samples may be determined by reference to the curve. A similar calibration curve was made for pentaborane, and could be made for other materials.

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Freezing Points in Determination of Product Purity

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Impurities which are uneconomical to remove from industrial products generally form ideal systems with the compound being produced. Freezing and melting points can thus be used for quantitative analysis of materials of lower purity than is generally realized. The cryoscopic method of analysis is briefly, but critically, reviewed on this basis, possible sources of error are discussed, and some applications of the method to industrial products are presented. A versatile, new automatic freezing point apparatus which was developed in this laboratory is described. Its operation is based on the principle of maintaining a small constant temperature differential between the sample and the surrounding bath, so that constant, controlled rates of heat transfer are obtained. The temperature of the sample is plotted automatically with an accuracy of ±0.01° C. over the range −40° to +200° C. This range can readily be extended to cover any portion or all of the range −180° to +660° C., so that the temperature recorder should find many other research applications in addition to the determination of product purity.

THE measurement of freezing and melting points has long been accepted as a qualitative method for estimating the purity of materials, but some of the quantitative applications of cryoscopic measurements seem to have been neglected by industry. Two factors appear to be largely responsible for this: the need for automatic temperature-recording equipment of suitable accuracy and dependability, and the difficulty in treating nonideal systems quantitatively. Recent advances in resistance thermometer instrumentation give promise that temperature recorders suitable for the determination of product purity from time-temperature curves will soon be available commercially at a cost comparable with other precision analytical instruments. It is also gradually being recognized that the impurities which are uneconomical to remove from organic chemicals of industrial interest will probably form ideal systems because of their structural similarity to the desired product.

The importance of the cryoscopic method lies in the fact that it detects the sum total of impurities in a sample and becomes more reliable as the purity approaches 100%, the very region in which most analytical methods become less exact. On the other hand, the method is not applicable if the material cannot be solidified, if the material decomposes at its melting point, or if the impurities are not soluble in the melt at the freezing temperature. In addition, the cryoscopic method will not generally divulge the chemical identity of the impurities. As is true with other analytical techniques, the cryoscopic method is not a cure-all, but a recognition of its limitations serves only to increase the confidence in the applications to which it may be put.

The purpose of this paper is to summarize the factors that must be considered in determinations of purity by the cryoscopic method, to point out how nearly most organic systems of industrial interest approach ideal behavior, and to describe a new freezing point apparatus and recording equipment developed and used in this laboratory.

The measurement of purity cryoscopically may be considered to involve three general problems:

Measurement of the freezing point for pure material.
Determination of the relationship between freezing point and purity.
Elimination of errors in the application of the method.

The first problem, characterization of the freezing point, T_0, for the pure material, involves either the preparation of a highly purified reference sample or the analytical estimation of T_0 from the shape of the freezing or melting curve of a somewhat impure sample. Once T_0 is known with sufficient reliability, impure samples may be readily analyzed for purity by a simple freezing point measurement, provided that the relationship between the purity and freezing point is known or may be predicted. Generally, such composition–freezing point calibration curves are experimentally determined, but many organic systems of industrial interest are so nearly ideal that the relationship may be successfully calculated. The third problem in cryoscopic measurements is to eliminate any significant errors in the determination of freezing points and purities due to slow approach to equilibrium, polymorphic changes, nonideal behavior, and the formation of solid solutions, compounds, or eutectics. Each of the foregoing three problems is considered briefly below.

ESTIMATION OF T_0

One of the most useful applications of the cryoscopic method involves the estimation of T_0, the freezing point of 100% pure material, using only a moderately pure sample. Once T_0 is known, the purity of this somewhat impure sample can be readily deduced from its measured freezing point, T_f, without the necessity of preparing a highly purified reference material. This is especially valuable in checking the purities of new synthetic chemicals, of isomeric mixtures that are difficult to separate and of reference standards that are used in other methods of analysis such as spectrophotometry and titrimetry.

A number of different techniques for estimating T_0 have been proposed by Mair *et al.* (*6*), Aston *et al.* (*1*, *2*), Herington and Handley (*4*), Stull (*7*), and others, but all are modifications of the fundamental principles originally formulated by White in 1920 (*10*).

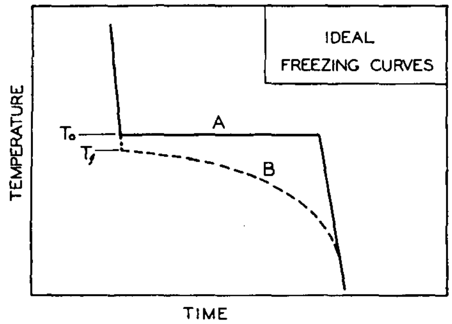

Figure 1. Ideal Freezing Curves at Constant Rates of Heat Transfer

A. **100% pure sample**
B. **Impure sample of same material**

The equilibrium time-temperature freezing curve for a 100% pure material may be represented by curve *A* in Figure 1. As heat is removed at a constant rate from the liquid sample, the temperature falls linearly with time until the freezing point T_0, is reached. Pure solid then freezes out and the phase rule requires that the temperature remain constant until the sample is entirely frozen. The further removal of heat then merely cools the solid. Curve *B* represents the equilibrium freezing curve for a somewhat impure sample of the same material cooled at the same rate of heat transfer as in curve *A*. Solid freezes out below T_0 at some temperature T_f. As pure solid is removed from the liquid at a constant rate, the liquid remaining becomes enriched in the impurities and the temperature continues to fall at a gradually increasing rate until the sample is entirely frozen. Equilibrium melting curves are merely mirror images of freezing curves.

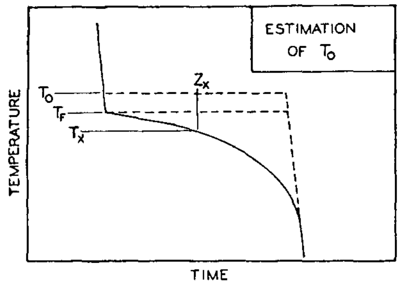

Figure 2. Freezing Curve for Impure Sample, Showing How T_0 May Be Estimated

The curves of Figure 1 are reproduced in Figure 2 to show how T_0 may be estimated.

If heat is removed from the sample at a constant rate during the freezing process, the extension of the portion of the continuous line which represents cooling solid until it intersects the dotted horizontal T_f line approximates the time at which the sample would have been completely frozen if no cooling had occurred. This means that the length of any fraction of the dotted T_f line is very nearly proportional to the fraction of the sample frozen. If Z_x is chosen as the midpoint of the dotted T_f line, T_x represents the temperature at which the sample is half frozen and the concentration of the impurities remaining in the liquid is twice as great as in the original sample. Now, if the impurity concentration is sufficiently low so that it is proportional to the freezing point lowering, $(T_f - T_x)$ is exactly equal to $(T_0 - T_f)$ and T_0 may be readily estimated.

Rossini and his coworkers (*3*, *9*) have developed analytical equations for determining $T_0 - T_f$ from the shape of the time-temperature freezing and melting curves, so that the entire curves need not be determined, but the assumption of thermodynamic ideality of the solutions is still made and, as it is a difference method, temperatures must be measured with greater accuracy than is necessary when the entire curve is measured.

In the calorimetric method of Aston and his coworkers (*1*), the fraction of the sample that is melted is determined from the accurately measured heat input, and this function is related to the equilibrium temperature, either graphically or analytically, as in the time-temperature methods. Although the calorimetric method is probably capable of greater accuracy, it is not so rapid or as generally applicable as the time-temperature methods.

CALIBRATION CURVES OF FREEZING POINT VERSUS PURITY

Once T_0 is estimated with sufficient accuracy using a moderately pure sample, the purity of this and any other sample of the same material may be determined using only the value for the freezing (or melting) point, provided that the relation between freezing point and purity is known.

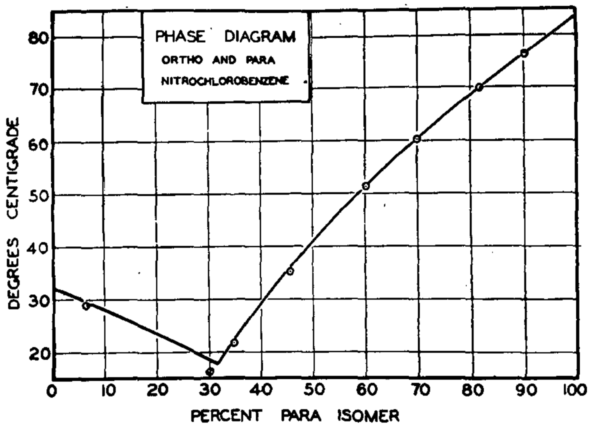

Figure 3. Comparison of Calculated (Solid Lines) and Experimental (Circles) Solid-Liquid Phase Diagrams

For thermodynamically ideal systems the freezing temperature, T_f, of a mixture is related to the purity and T_0 by Equation 1, the well-known equation for solid-liquid equilibrium:

$$\ln \frac{P}{100} = -\frac{L_f}{RT_0}\frac{(T_0 - T_f)}{T_f} \tag{1}$$

where P is the mole per cent purity, T_0 and T_f are absolute temperatures as already defined, R is the molar gas constant, and L_f is the molar heat of fusion. P and L_f relate to the solid phase freezing out whether it is present in excess or not. Literature values for L_f are frequently not available, in which case L_f may be measured calorimetrically or cryoscopically. The purity P is relatively insensitive to changes in the value used for L_f so that L_f can often be estimated with sufficient accuracy by the use of the rule that the entropy of fusion, L_f/T_0, is constant for chemically similar substances. This relationship appears to hold especially well for aromatic chemicals.

The only assumptions involved in the derivation of Equation 1 are:

1. L_f is constant over the temperature range T_0 to T_f
2. Only one component freezes out
3. The solution is thermodynamically ideal

The first assumption introduces very little error because of the relatively small temperature ranges generally involved. The second assumption, however, requires that no eutectics, compounds, or solid solutions separate out; the influence of these is discussed later.

The last assumption is generally valid because the impurities which are most difficult to remove from organic materials are usually those which are structurally similar to the product that is desired—e.g., isomers and homologs—yet these are the very materials most likely to form ideal mixtures with the major component. An example of this is the system, *o*- and *p*-nitrochlorobenzene, which is represented in Figure 3. The solid curves were calculated from Equation 1, while the circles represent experimental data reported by Holleman (*5*). The agreement is very nearly perfect even as to the freezing temperature and composition of the eutectic. Crude coal-tar naphthalene is another example. This material contains a mixture of aromatic and aliphatic impurities, yet behaves as if it were very nearly ideal up to impurity concentrations as high as 60%, as shown in Figure 4. In this example the creosote oil was carefully fractionated to remove the naphthalene, and the average molecular weight of the naphthalene-free oil was determined in *p*-nitrochlorobenzene. The solid line was calculated using this value for the molecular weight of the oil and the circles represent experimentally determined points upon the addition of the oil to pure naphthalene.

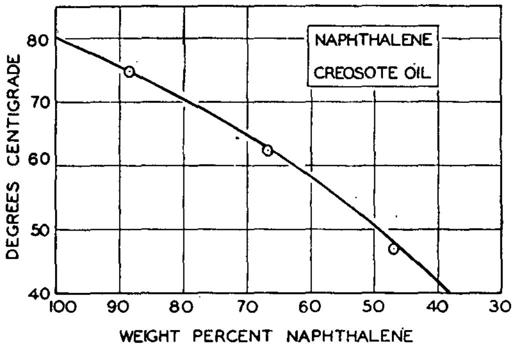

Figure 4. Comparison of Calculated (Solid Line) and Experimental (Circles) Freezing Point Diagram for Naphthalene Creosote Oil

Many organic systems of commercial interest such as mixed xylenes, dichlorobenzenes, gasoline aliphatics, etc., behave ideally even when the impurity concentrations are large. Thus, once T_0 and L_f are known, the freezing point–purity relationship may be calculated and one or two experimental points will usually suffice to verify the ideality of the system or at least will permit adjustment of the calibration curve for slight deviations from ideality.

POSSIBLE SOURCES OF ERRORS

Attainment of Equilibrium. Mathematical analysis of time-temperature freezing and melting curves for the estimation of T_0 requires adequate attainment of equilibrium along the entire solid-liquid curve. A typical example of such an equilibrium curve is shown in Figure 5, which presents an experimentally determined curve for a highly purified sample of cyanuric chloride. On the other hand, the experimentally determined curve for a sample of diethyl dithiophosphoric acid which is reproduced in Figure 6 shows that in this case supercooling was significant and recovery of equilibrium was slow, even though the sample was well seeded.

The temperature maximum attained after supercooling and represented by T_s in Figure 6 is often used to characterize the freezing points of samples, yet the true equilibrium value is represented by T_f. This difference can become large as the purity decreases and supercooling becomes marked. In addition, materials such as *o*-nitrochlorobenzene and *o*-nitrodiphenylamine, for example, were found to require an hour or more to equilibrate after supercooling, even when extremely pure and well seeded.

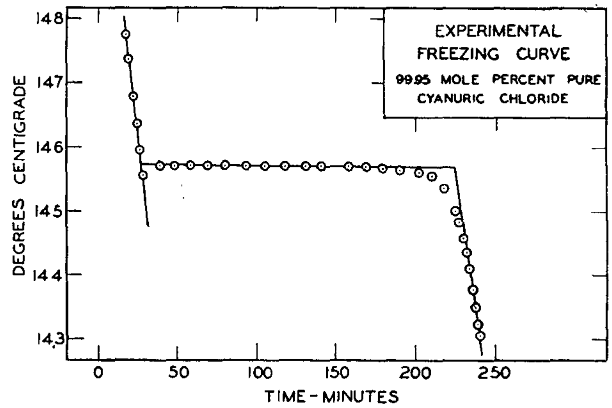

Figure 5. Experimental Freezing Curve for Material of High Purity

A number of techniques may be used to detect nonequilibrium conditions. Both freezing and melting curves can be run on the same sample, in which case any difference in the temperature of the transition is a measure of the deviation from equilibrium. The true equilibrium value is not always the mean of these two transition temperatures. A useful procedure for correcting for nonequilibrium conditions is to determine the freezing or melting curves at two different rates of heat transfer and then to extrapolate the resulting transition temperatures linearly to zero rate of heat transfer. The "constant temperature differential" (CTD) freezing point apparatus developed in this laboratory and described under Apparatus is admirably adapted for this purpose. When the attainment of equilibrium is impractically slow, the constant temperature differential apparatus is especially useful, because heat transfer to or from the sample can be reduced to zero by thermostating the outside bath at the sample temperature until equilibration is complete. The rate of approach of the sample to equilibrium may be determined by following changes in the sample temperature under adiabatic conditions.

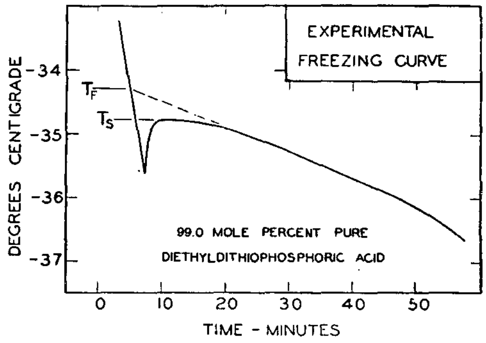

Figure 6. Experimental Freezing Curve for Somewhat Impure Material

Eutectic Formation. The cryoscopic behavior of a eutectic mixture is identical with that for a pure compound. In fact, the shape of a eutectic freezing or melting curve may in some cases be used to determine other impurities than those forming the eutectic—e.g., for determining the amount of a meta isomer in an essentially eutectic mixture of ortho, para isomers. On the other hand, the presence of undetected eutectic solid phases flattens the solid-liquid portions of the time-temperature curves and leads to anomalously high purities. Thus, if the sample to be analyzed happens to contain exactly a eutectic mixture of impurities, none of them will be detected from the freezing curve. It can be shown from Equation 1, however, that this is a highly improbable situation in the 90 to 100% purity range, because an organic chemical that freezes between −40° and +200° C. can form eutectics with as low as 10% of an impurity only when the freezing point of the impurity itself is at least 100° higher than the compound of interest. This difference in freezing points must become even greater when the impurity concentration in the eutectic becomes less, requiring considerable chemical dissimilarity between the compounds. Thus the possibility of encountering eutectic mixtures in the 90 to 100% purity range becomes small when several different methods of purification are employed.

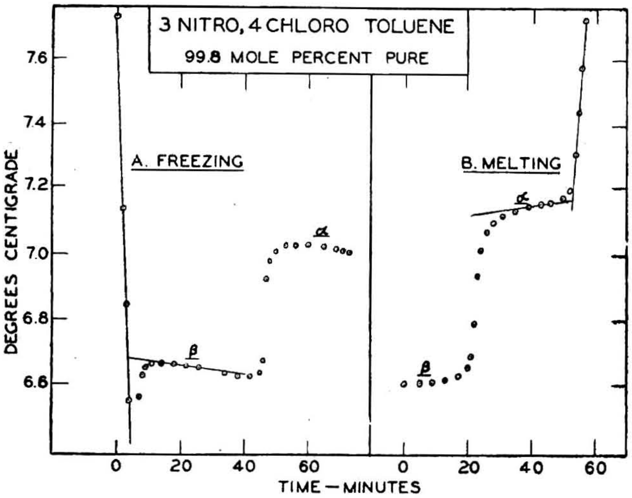

Figure 7. Experimental Freezing and Melting Curves for Material Exhibiting Polymorphic Transition

When the amount of an impurity in a sample exceeds the eutectic composition, owing to a high impurity concentration or to marked deviations from ideal behavior, the impurity will be the first solid phase to freeze out. The temperature coefficient of solubility for the impurity must be high when the impurity concentration in the eutectic is less than 20%, however, so the precipitation of the impurity will not affect the slope of the liquid portion of the freezing curve perceptibly and may not be detected. The presence of the impurity solid phase can easily be found by noting the turbidity it produces in the sample just above the observed eutectic break. If the composition of the sample is near the eutectic composition, the time-temperature curve of the eutectic may be used to determine the concentration of any other impurities.

Solid Solution Formation. The cryoscopic method of analysis is based on the separation of a single, pure, solid phase. If any of the impurities in a sample form a solid solution with the major component, the relationship expressed in Equation 1 is no longer valid, unless it is adjusted by a factor dependent upon the distribution coefficient of the components between the solid and liquid phases. This distribution coefficient is generally not known, of course, so no correction can be made. Fortunately, in organic chemical systems the appearance of solid solutions is much more infrequent than the more normal eutectic type behavior. In addition, several methods are available for detecting the presence of solid solutions. If the impurity forming the solid solution is present in appreciable quantity, it may be detected from a flattening in the time-temperature curve. In most cases the impurities likely to be present in appreciable quantities are known from the preparative method used to obtain the sample, so that these impurities may be added to the sample in known amounts and anomalous behavior detected from abnormal changes in the freezing point.

All major sources of error in the cryoscopic method, including the appearance of solid solutions, tend to yield abnormally high purities. Thus, should solid solutions be present and remain undetected, the impurities that are measured represent a minimum value.

Polymorphic Behavior. Many organic materials can exist in two or more crystalline states, each form exhibiting its own freezing point. When the freezing points differ widely, no difficulty is encountered in cryoscopic methods of analysis, because it is immediately apparent from the freezing temperature which form is separating out. When, however, the freezing points of the polymorphs lie close together, the purity analysis will be in error if the wrong solid phase appears. An unusual example of this was found when freezing and melting curves were run at constant rates of heat transfer on a sample of 3-nitro-4-chlorotoluene. Two crystalline modifications appeared which froze only 0.5° C. apart, as demonstrated by the time-temperature curves presented in Figure 7. After approximately 30 minutes near the freezing point, the metastable β modification was observed to convert spontaneously to the α form.

Other Sources of Error. Compound formation between an impurity and the material being analyzed introduces two sources of error, one due to the large deviations from ideal behavior and the other due to the anomalous increase in the molar concentration of the impurity. Here again the very factors that introduce errors in the cryoscopic method tend to simplify the separation of the complicating impurities, so that the probability of error is greatly reduced. In any case, however, care must be exercised in applying the cryoscopic method to strongly acidic or basic materials.

In most analyses the weight per cent impurity is desired rather than mole per cent. When the average molecular weight of the impurities is known or may be approximated with sufficient accuracy, the conversion between the two concentration units is readily calculated. When, however, the average molecular weight of the impurities is unknown, it is sometimes practical to determine the average molecular weight of the entire sample in another material, and to use this value to convert from mole per cent to weight per cent.

CONSTANT TEMPERATURE DIFFERENTIAL APPARATUS

In the classical Beckman method of measuring freezing or melting curves, the stirred sample is separated from a bath of fairly constant temperature by an air space which serves to regulate the rate of heat transfer. As the temperature of the sample changes, the temperature difference between the bath and the sample also changes and the rate of heat transfer is, of course, continually varying. Rossini (*6*) and his coworkers at the National Bureau of Standards reduced the magnitude of this variation by using a large temperature differential (of the order of 50° to 100° C.) between the bath and the sample and evacuating the space in between. This requires that pressures of the order of 1 to 10 microns be maintained constant throughout the experiment. Stull (*7*) circumvented the problem of maintaining uniform low pressures by using several Dewar-type sample tubes presealed at the desired degree of vacuum.

Aston (*1*) and his coworkers applied known increments of heat to the frozen sample in a calorimeter and measured the temperature rise after each addition. Thus, instead of plotting time against temperature, the fraction melted was plotted against temperature. There is probably little to choose between the calorimetric method and the National Bureau of Standards method, because both have applications to which they are peculiarly suited.

Another solution to the problem of maintaining constant rates of heat transfer is to use an atmospheric pressure air baffle as in the Beckman method but to maintain a relatively small (0° to 10° C.) constant temperature differential between the sample and the bath. Although at first glance this may appear to be unduly difficult to accomplish, preliminary experiments in this laboratory indicated that such was not the case in the temperature range of interest—namely, −40° to +200° C. As a result, the manually controlled apparatus shown in Figure 8 was developed.

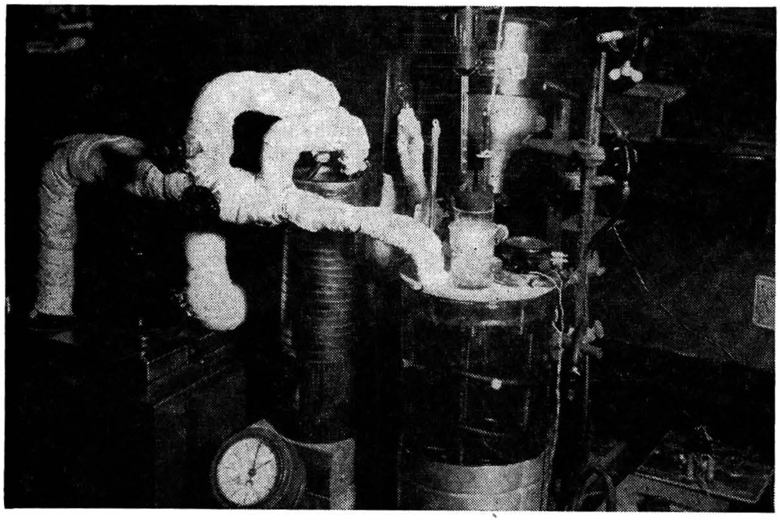

Figure 8. Constant Temperature Differential Freezing Point Apparatus

The sample tube consisted of a glass tube 35 mm. in outside diameter and 310 mm. long, constricted to 25 mm. at the bottom. The constriction permitted sample volumes from 5 to 40 ml. to be used in the same tube. The top of the sample tube contained a rubber stopper with openings for the glass-spiral reciprocating-type stirrer, for the platinum resistance thermometer, for introducing an inert atmosphere, and for seeding or sampling the contents of the tube. A male 45/50 ₸ joint near the top of the sample tube fitted the female joint at the top of a glass jacket 45 mm. in outside diameter, so that a 3-mm. air gap separated the two tubes. The air gap between the two tubes was maintained at atmospheric pressure by means of a small opening near the top of the sample tube.

The bath surrounding the jacket consisted of a 4-liter, unsilvered Dewar containing a stirrer, thermoregulator, thermometer, electrical heating coil, and coil for circulating a cooling fluid. *cis*-Decalin was used for both the bath liquid and the circulating fluid because of its low viscosity at −40° C., low freezing point (−125° C.), and high boiling point (193° C.). The circulating fluid was cooled to temperatures as low as −25° C. in an Aminco refrigerated bath and, when needed, the precooled fluid was further cooled to −80° C. by passing it through a Dewar containing a dry ice–decalin mixture. The path and rate of flow of the circulating fluid were controlled by means of two 0.25-inch needle valves. When bath temperatures above 170° C. were desired, the *cis*-Decalin bath fluid was replaced with mineral oil.

For bath temperatures below about 50° C. the cooling fluid was circulated at a constant rate, and the bath temperature was controlled by adjusting the electrical heat input. Above 50° C. the circulating coolant was generally not needed. For temperature differentials of less than 2° C. between the bath and the sample, heat was applied continuously, the rate being controlled by adjusting the applied voltage. For larger temperature differentials, a thermoregulator was used, the setting being adjusted at regular intervals to follow changes in the sample temperature.

During a run, the sample and bath temperatures were measured at regular time intervals and recorded. The difference was calculated and the heater voltage or the thermoregulator setting was adjusted to maintain the desired temperature differential. When readings were taken every minute, sufficient time was available to plot the time-temperature curves in addition to carrying out the other control operations.

The freezing and melting curves shown in Figure 9 were obtained on the same sample at identical temperature differentials using the constant temperature differential apparatus. The melting curve has been reversed on the time scale for ease of comparison. The equilibrium portions of the curves were perfectly linear, so that it was a simple matter to interpolate to the true freezing and melting points, even though the slopes of the lines did not differ greatly. The difference of 0.1° C. between the observed freezing and melting points showed that the samples were not perfectly equilibrated even at the low rates of heat transfer used in these experiments. When marked deviations from equilibrium or polymorphic changes occurred, the constant temperature differential apparatus proved to be especially useful, because the rate of heat transfer could be rapidly reduced to zero until equilibrium was established, as evidenced by a constant sample temperature, and then the time-temperature curve could be continued at the original rate of heat transfer.

AUTOMATIC APPARATUS

In order to simplify the operation and extend the usefulness of the constant temperature differential apparatus, automatic temperature recording and controlling equipment was developed in cooperation with the Thwing-Albert Instrument Co. Two Model L-50 resistance recorders were modified, one to record the sample temperature (absolute recorder) and the other to record and control the temperature difference between the sample and the bath (differential controller). As a detailed discussion of the equipment is being planned for a future publication, only a general outline of the construction is presented here.

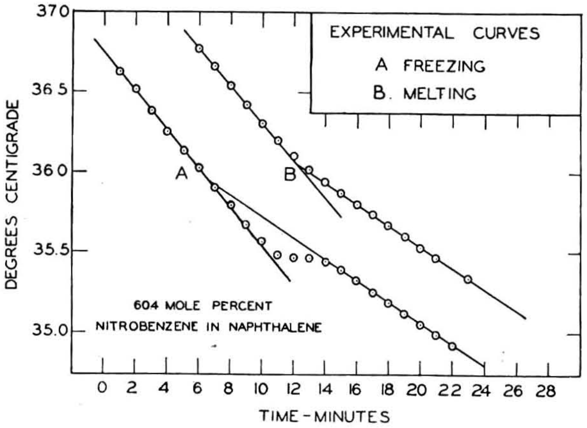

Figure 9. Freezing and Melting Curves Obtained from Same Sample

CTD apparatus used. Magnitude of temperature differential was same for both curves. For clarity, time scale for melting curve has been reversed

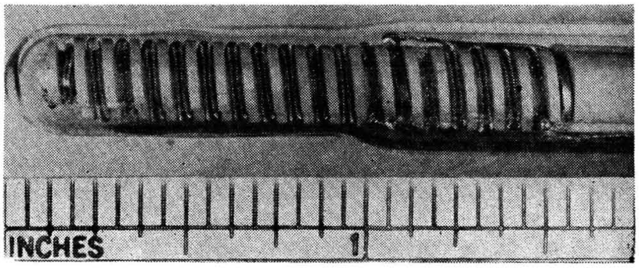

Figure 10. Compound Platinum Resistance Thermometer Element for Immersion in Sample

The pioneering work of Stull (*8*) in recording resistance thermometry served as a valuable guide in designing the absolute recorder.

The recorders were operated by the converted and amplified direct current signal from the Wheatstone bridge circuits. Only 1.7-mil current passed through the thermometers in order to eliminate errors due to heating. The compound resistance element shown in Figure 10 was immersed in the sample. The lower two thirds of this element consisted of a 125-ohm platinum coil which served as one arm of the bridge circuit in the absolute recorder. The upper, 60-ohm section and another identical 60-ohm section, which was immersed in the outside bath, served as opposing arms in the differential controller bridge circuit.

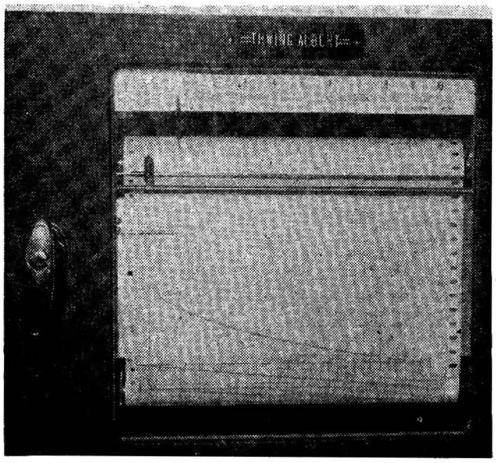

Figure 11. Precision Absolute Temperature Recorder

The temperature differential between the bath and the sample was fixed by setting a control pointer on the differential controller. The pen carriage operated a microswitch fixed to the control pointer, and the microswitch, in turn, controlled the heat input to the bath. Full scale temperature differential ranges of ±2°, 5°, 10°, and 20° C. could be chosen by switching in the proper slide-wire shunts.

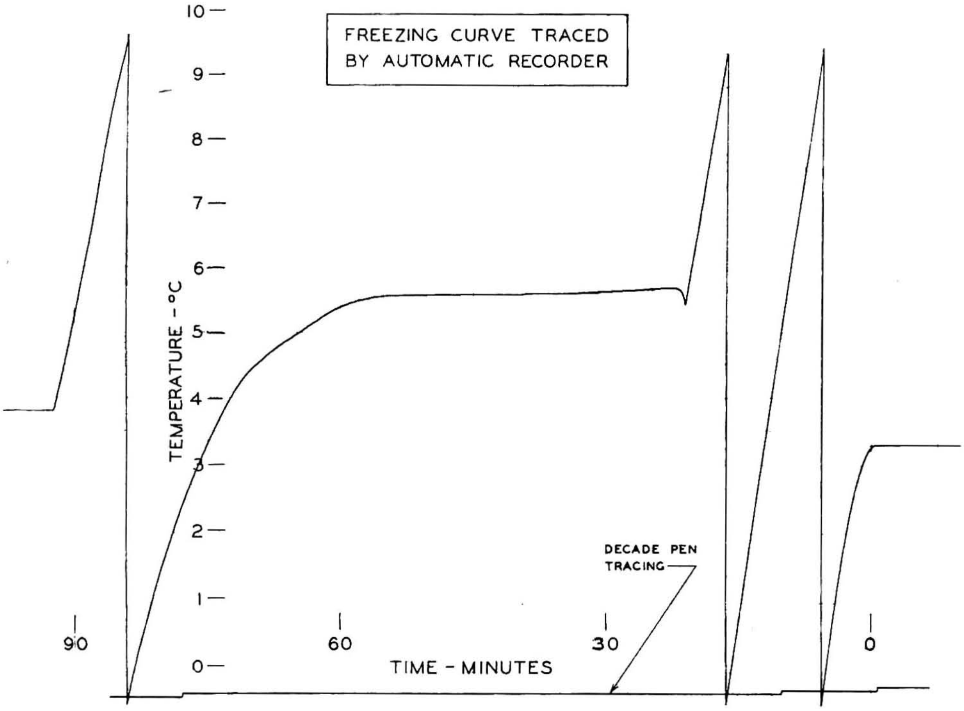

Figure 12. Curve Drawn by Absolute Temperature Recorder for Plant Sample of Nitrobenzene

The absolute recorder is shown in Figure 11.

The full scale range of the instrument was 10° C. with 0.5° overshoot at each end. Ranges were automatically shifted at each end of the pen travel and the decade in use was indicated by a second pen, which was displaced slightly on the time scale. In order to record temperatures abolutely over all the decades, the slight nonlinearity of the temperature coefficient of platinum was compensated for by shifting both ratio arms in the bridge circuit for each decade. Switching both ratio arms also tended to cancel any errors due to contact resistances in the switches. By choosing proper values for the ratio arm resistors, temperatures were recorded with an accuracy of ±0.01° C. throughout the full temperature range of −40° to +200° C. This range can, of course, be readily extended to cover any portion or all of the platinum thermometer range of −190° to +660° C. The stability and sensitivity of the absolute recorder were both better than 0.01° C.

An automatically recorded freezing curve for a plant sample of nitrobenzene is presented in Figure 12. Temperature is shown vertically and time horizontally from right to left. As the temperature of the liquid sample fell, the ranges were shifted automatically until the sample began to freeze in the range shown on the vertical scale. The temperature of the sample increased, owing to recovery from supercooling, and then remained constant until the sample was almost completely frozen. When the sample was frozen solid, the temperature decreased rapidly and, at the lower limit of the scale, the instrument shifted to the next lower range. The pen tracing at the bottom of Figure 12 indicated the temperature decade in use.

The advantages of accurate temperature records, as compared with visually observed and manually recorded data, for characterizing the freezing points of industrial products are at once apparent. In addition, temperature recorders with an accuracy of 0.01° C. should also find many research and production applications in fields other than that of cryoscopic measurements.

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Qualitative Separations by Two-Way and Three-Way Electrochromatography

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Differential electrical migration in paper moistened with one solvent followed by transverse electromigration after variation of the solvent has been tested as a qualitative analytical method for the separation of the cations of the common qualitative groups. This method, employed with various solvents and absorptive phases, has served for the separation of very small quantities of the mixtures. Its effectiveness depends upon the concentration of the ions to be resolved, the methods for the detection of the resolved ions, and the presence of various complex-forming solutes. The results reveal that complexes formed between metal ions and various organic solutes must be in dynamic equilibrium. They demonstrate that separations based upon electrical migration are more variable than those dependent upon the flow of solvent. The sequences of the electromigration zones may be varied so that absolute separations of many ions are possible. Information obtained by these methods is applicable to the continuous separation of ions by the combination of electromigration plus flow of solvent.

CROSS-CAPILLARY analysis (*9*) or two-dimensional chromatography (*2*) is a widely applicable analytical tool (*8*). In this two-way method a mixture of solutes, applied as a spot near one corner of a sheet of paper, is washed or developed with one solvent, and this initial, one-way development is followed by transverse irrigation with another solvent. The separations depend upon differential migration of the solutes in the polyphase system.

Flow of electrical current without flow of solvent has also been employed for the resolution of mixtures by one-way differential migration of the solutes in various polyphase chromatographic systems such as columns of moist porous adsorbents (*8, 12, 13, 16*), columns of ion exchange resins (*11*), strips of moist filter paper (*3, 4, 7, 10, 12, 17–19*), and stacks of filter paper (*5*). Simultaneous flow of solvent and of electrical current has been employed for two-way electrochromatographic development in sheets of paper (*6, 17*). These separations are known as analysis by electrochromatography (*6, 12, 17*), by electromigration (*11*), by electrophoresis or ionophoresis (*3, 4, 18, 19*), and by ionography (*10, 12*).

Through the successive use of different solvents in sheets of porous media, such as sheets of cellulose or glass-fiber paper or cells of Celite, electromigration has now proved widely applicable in two-way and three-way separations. In most experiments reported here, flow of electrical current through absorptive sheets moistened with one solvent was followed by transverse flow of electrical current in the presence of another solvent. For the three-way development, a section of the two-way separation was placed in contact with the edges of two rectangular sheets of paper that were moistened with the third solvent. Variation of pH and the addition of complex-forming reagents have proved especially effective in the electrophoretic separation of many mixtures, and these variations were usually achieved quickly without removal of the first solvent.

METHODS

The separations by differential electrical migration which are reported here represent an amplification of previous experience in this laboratory (*17*). They were performed with paper strips (*12, 17*) or with paper squares, usually about 20 × 20 or 30 × 30 cm., cut from thick, soft, commercial filter paper. Much larger sheets, 55 × 55 cm. and 20 × 200 cm., are being tested.

Eaton-Dikeman paper, Grade 301, 0.030 or 0.052 inch thick, or Grade 320, 0.1 inch thick, usually gave satisfactory separations. Grade 625 was less satisfactory. Some of the papers, such as Grade 625, contained impurities (probably chlorides) that migrated to the anode and that formed precipitates with silver and lead ions in 0.1 *M* lactic acid. This precipitate was not formed with silver ions in 4 *M* ammonia. The impurities in the paper were removed by electromigration in a large volume of dilute solution of ammonia or of volatile organic acids, the current flowing at right angles to the plane of the paper.

Glass-fiber paper was obtained from the Office of Naval Research (*1*). This paper did not contain impurities that combined with silver ions in acid solution. In the presence of ammonia, it had much less affinity for cupric ions than cellulose.

For comparison of the migration rates of various ions, the apparatus shown in Figures 1 and 2 has proved convenient. For one-way and two-way separations, the arrangements shown in Figure 3 have been used most. In both arrangements the paper squares were placed on a horizontal plastic, glass, or porcelain plate or on a water-cooled glass tank. This paper was treated with an excess of the electrolytic solvent, and the unabsorbed liquid was removed with absorptive tissue paper (Kleenex). Formation of acidic and basic zones at the electrodes was reduced by the use of weak acids or bases as the electrolytes (*17*), thus eliminating the need for the electrode vessels and buffer solutions commonly employed for one-way electrophoresis in paper (*3, 4, 7, 10, 17–19*).

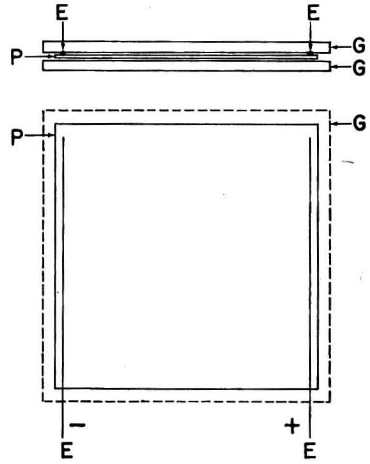

Figure 1. Cell for Two-Way and Three-Way Electromigration

Above. **Cross section**
Below. **Top view**
E, **platinum wire electrodes**
G, **glass panes**
P, **paper**

Solutions (10 to 50 microliters) of the mixtures to be examined (0.005 to 0.05 *M*) were placed on penciled areas of the paper with a fine-tipped pipet. Platinum wires (8 to 20 mils) were placed along opposite sides of the paper square and were held in place by a square plastic or glass plate, which was slightly larger than the paper. This square cover rested on the wire electrodes and scarcely touched the paper itself (Figure 1). Potential (160 to 400 volts) was applied to the electrodes for about 15 to 30 minutes for each development.

For the detection of colorless ions separated by electrophoresis, the electrical current was discontinued, the upper glass plate was removed, and reagents were applied to the paper (as gases, as sprays, or by brushing). Ions separated in the paper were often detectable by pressing the moist paper against dry paper, such as pH test paper, that had been impregnated with the reagent.

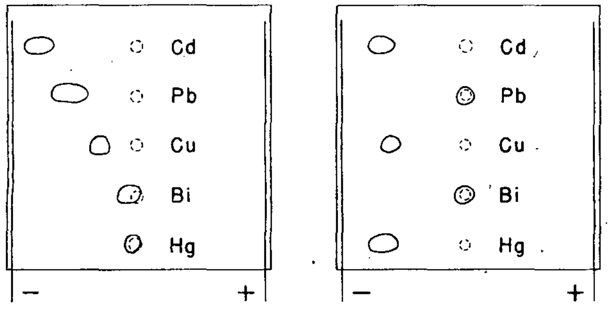

Figure 2. Migration of Copper Group Cations (Each about 0.005 M) in Paper (20 × 20 Cm.)

Left: **In 0.1 M lactic acid**
Right. **In 4 M ammonia plus 0.1 M lactic acid**
Ions located with hydrogen sulfide

They were also detectable by placing the opposite edges of a section of the chromatogram in contact with edges of two moist sheets of the impregnated paper so that the ions could be driven into the treated paper with electrical current, the arrangement being analogous to that shown in Figure 4. As an example, opposite edges of a section of paper containing separate zones of nickel and copper ions (0.001 to 0.0001 M) in tartaric acid (1.5%) plus triethylamine (2.0%) were placed in contact with the edges of two squares of paper impregnated with dithio-oxamide and moistened with the tartaric acid plus triethylamine. When the electrical current was passed through the papers for several minutes, the copper and nickel ions migrated toward the anode and reacted with the dithio-oxamide, yielding very narrow, intensely colored zones of the dithio-oxamide reaction products.

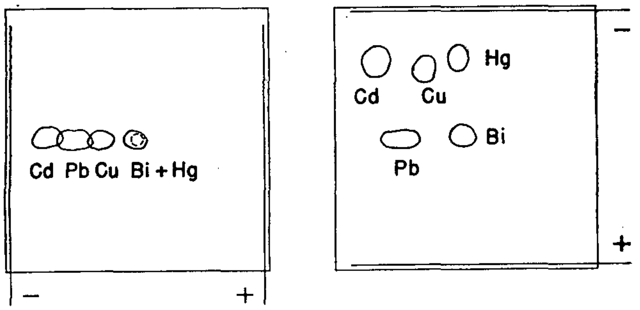

Figure 3. One-Way Migration of Copper Group Cations in 0.1 M Lactic Acid (*left*) and One-Way Separation, as at Left, after Treatment with Ammonia and Transverse Development (*right*)

Ions located with hydrogen sulfide

Paper impregnated with various reagents has facilitated the electrophoretic separation of many ions. With paper impregnated with dithio-oxamide and with 1.5% tartaric acid as solvent, cupric and silver ions were precipitated and, along with ferric ions, did not migrate, whereas cobalt and nickel ions migrated rapidly to the cathode. With 1.5% tartaric acid plus 2% triethylamine as solvent, cobalt, nickel, copper, and silver were precipitated, but ferric ions migrated rapidly to the anode. This variation of solvents, reagents, and pH provides a variety of conditions for the separation of ionic mixtures.

From the relative migration rates of the ions (Figure 2), the suitability of various solvents and reagents for the two-way and three-way separations was estimated. These comparisons also provided a basis for estimation of the relative positions of the ions in the two-way and three-way separations. In the presence of lactic acid, for example (Figure 2), cadmium, lead, and copper migrated at different rates and should be partially separated from one another and from bismuth and mercury by one-way migration. This was confirmed as shown by Figure 3. In the presence of ammonia plus lactic acid (Figure 2), cadmium, copper, and mercury migrated faster than lead and bismuth. If, therefore, a one-way development of these five cations in dilute lactic acid were submitted to a transverse development in the presence of ammonia, cadmium and copper should be separated from lead, and mercury should be separated from bismuth. This was confirmed experimentally as indicated by Figure 3.

Variation of the solvent for two-way separations has been achieved most easily by exposure of the moist paper, after one-way development, to a gas. In the example illustrated by Figure 3, the moist paper, after one-way development, was placed on a horizontal glass rack over concentrated ammonium hydroxide in a closed vessel. Alternatively, gaseous ammonia may be passed through the vessel. The solvent has also been varied by cutting a small rectangular section from the one-way or two-way chromatogram and by placing this section between two strips or sheets of paper moistened with the second solvent or third solvent (Figure 4). For this procedure, the one-way development may also be carried out in a paper strip (*12, 17*). Occasionally the papers were dried and then sprayed with the second or third solvent until moist.

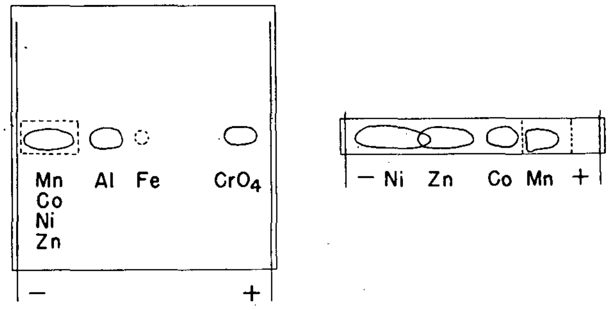

Figure 4. One-Way Migration of Iron Group Cations with 0.1 M Lactic Acid (*left*) and Two-Way Migration after Section from One-Way Separation (*left*) Was Exposed to Ammonia Vapor and to Transverse Flow of Electrical Current (*right*)

Ions located with aluminon plus acetic acid, diphenylthiocarbazide, and dithio-oxamide

In order to follow the course of the separations, several sheets of filter paper were often employed for the initial development. Intimate contact between the several moistened sheets was established by rolling them with a piece of glass tubing shaped like a rolling pin. The mixture was added, and the development was then carried out as already described. After a suitable period, the uppermost sheet of paper was removed, and the progress of the separation in this paper was determined with reagents. When the ions had been carried about two thirds of the way across the paper, the solvent was varied, and the transverse development was undertaken.

SHAPE OF MIGRATION ZONES

At low concentration, most solutes formed rather homogeneous migration zones with well-defined boundaries. With increasing amount and concentration of a solute, the leading boundary of the zone moved faster than the trailing boundary so that the zones lengthened rapidly as indicated by Tables I and II. In these experiments, Eaton-Dikeman paper, Grade 301, 0.052 inch thick, 13 × 20 cm., was placed on a glass plate; it was saturated with the solvent, and 25-microliter portions of the solutions of cupric nitrate were added to separate regions as illustrated by Figure 2. A potential of 160 volts was then applied to the electrodes held 19 cm. apart by the glass cover. After passage of the current (about 16 ma. with ammonia solutions and 20 ma. with lactic acid) for an hour, the position of the cupric ions was determined with dithio-oxamide in methanol. In either acidic or basic solutions, the migration rates of cupric ions at the leading boundaries increased with increasing concentration, whereas the migration rates of the trailing boundaries increased slightly with concentration and then decreased rapidly at the higher concentrations.

Table I. Concentration and Electromigration of Cupric Ions in 4 M Ammonia in Paper

Cupric Nitrate in 4 M Ammonia, M	Migration Leading Boundary, Cm.	Migration Trailing Boundary, Cm.	Length of Zone, Cm.
0.5	2.4	0.2	2.7
0.1	2.2	1.0	1.8
0.01	1.8	1.2	1.2
0.001	1.4	1.1	0.8
0.0001	1.3	1.1	0.7
0.00001	1.2	1.0	0.5

Table II. Concentration and Electromigration of Cupric Ions in 0.1 M Lactic Acid in Paper

Cupric Nitrate in Water, M	Migration Leading Boundary, Cm.	Migration Trailing Boundary, Cm.	Length of Zone, Cm.
0.5	6.0	0.6	6.2
0.1	5.5	3.5	3.0
0.01	5.0	4.4	1.4
0.001	4.4	4.3	0.9
0.0001	4.2	4.2	0.7
0.00001	3.8	3.9	0.4

The rapid migration of solutes at high concentration sometimes interfered with the isolation of minor, slower migrating constituents of mixtures. As an example in which 4 M ammonia was employed as solvent, nickel ions at a concentration of 1 M migrated nearly as fast as silver ions at 0.001 M, whereas nickel ions at 0.001 M migrated only about three fourths as fast as the silver or the 1 M nickel ions. In electromigration, the differential driving force of the electrical current (*12*) made possible the separation of 0.001 M silver ions from 0.1 M nickel ions, whereas by solvent flow in paper, the excess nickel was not absorbed and contaminated the silver unless a very long absorptive system was employed.

In order to compare chromatographic zones with the electromigration zones, 25-microliter portions of copper nitrate solutions were placed near one edge of a sheet of Eaton-Dikeman paper, the paper was placed between glass plates, and the edge nearest the spots was dipped into the solvent (*17*). After the solvent had risen 10 or 20 cm. (10 to 30 minutes), the paper was treated with dithio-oxamide. The migrations of the copper ions relative to the migration of the solvent, R, and the lengths of the zones of cupric ions, L, are summarized in Table III. In these experiments, the chromatographic migration and the length of the zones depended upon the amount of the cupric ions in the paper before development. With flow of ammonia especially, the zones became very long just as they did during electrophoresis, and the region of highest concentration remained near the trailing portion or the zone.

Table III. Concentration and Chromatographic Migration of Cupric Ions

Cupric Nitrate, M	4 M Ammonia[a]				0.1 M Lactic Acid			
	10 Cm.		20 Cm.		10 Cm.		20 Cm.	
	R	L	R	L	R	L	R	L
0.5	1.00	10.0	1.00	20.0	1.00	4.6	1.00	8.5
0.1	0.70	7.0	0.50	10.0	0.97	3.2	0.97	7.8
0.01	0.15	1.9	0.16	3.3	0.92	2.5	0.88	6.0
0.001	0.11	1.1	0.13	2.7	0.89	1.7	0.74	4.5
0.0001	0.09	0.9	0.11	2.3	0.87	1.1	0.65	3.0
0.00001	0.07	0.9	0.09	1.9	0.85	0.7	..	..

[a] R = distance moved by leading cupric ions ÷ distance moved by solvent; L = length of zone of cupric ions in centimeters after solvent migrated 10 or 20 cm.

When cupric nitrate in 4 M ammonia was allowed to flow directly into strips of filter paper, the rate of migration was much greater than that observed when 25-microliter portions of the solution in paper were washed with the fresh ammonia. For example, the R values for 0.5, 0.1, and 0.01 M cupric nitrate in 4 M ammonia were 1.00, 1.00, and 0.40, respectively.

Paper made from superfine glass fiber exhibited less adsorption capacity for cupric ions than paper made from cellulose fiber. In this glass paper, the trailing portions of the chromatographic zones were shorter than in cellulose paper. The widening of the electromigration zones due to rapid movement of the leading boundaries was similar to that observed in paper of cellulose fiber.

These experiments show that separations by electrophoresis and by conventional chromatography will be most effective at low concentration of the solutes (less than about 0.05 M for the major constituents). At these low concentrations the detection of the separated minor constituents by chemical reagents is often difficult. Among inorganic compounds, the use of radioactive tracers and the activation of resolved solutes by neutron irradiation show great promise for increasing the sensitivity of tests for the location and identification of the ions separated by differential migration methods.

SEQUENCE OF MIGRATION ZONES

In many of the separations by differential electromigration, the sequence of the separated ions was identical with the chromatographic sequence obtained by flow of solvent. In the presence of various complexing agents, however, the sequences of the ions varied greatly (*17*). An indication of the complexity of these effects may be gained by perusal of Tables IV and V.

As in the usual chromatographic separations, the sequence of the zones formed by electrolysis may serve as a basis for the description and identification of the solutes (*14*). If the original location of the mixture in the polyphase system is taken as the reference point, electrolysis yields many more positions of the zones than flow of solvent—for example, with two components, two sequences of the zones may be obtained by flow of solvent (*15*), but six different relative positions may be obtained by electrolysis. With cupric and nickel ions and with various solutes as complex-forming reagents, all these sequences have been obtained (Tables IV and V).

VARIABLE CONDITIONS

Just as in chromatography, there are two principal variables in the electrochromatographic separations. These variables are the solvent and the absorptive phase. Because the liquid phase is preferably a conducting solution, the number of solvents that may be employed is fewer than is usual with the common chromatographic methods. There are, however, almost limitless possibilities for variation of solvent by the use of solvent mixtures, by employment of various complex-forming solutes, and by variation of pH.

The number of absorptive phases that may be employed in these electrochromatographic separations is also very large. Cellulose paper has been widely used because of its availability and homogeneity. It has some disadvantages such as its capacity for the formation of complex ions with heavy metals. Glass-fiber paper (*1*) exhibits weaker complexing properties than cellulose paper, but the glass paper is very fragile when wet. A number of two-way separations have been made in flat beds of other absorptive materials such as Celite held between glass plates, and separations have also been made in cellulose paper and in glass paper that has been impregnated with absorptive substances such as silica gel or alumina.

MIGRATION FROM PRECIPITATES

After formation of a precipitate and under the influence of the electrical current, small quantities of the ion remaining in solution migrated rapidly, followed by fresh material supplied by dissolution of the precipitate. Under these conditions, the precipitate remained stationary yielding a long, dilute, leading zone. These leading zones often contained so little material that they could be detected only by the most sensitive chemical reagents or by radioactive tracers. As an example, copper nitrate added to a paper containing saturated anthranilic acid solution yielded a precipitate with so little copper ion in solution that flow of electrical current did not form a leading zone detectable with dithio-oxamide. But in the presence of 0.1 M lactic acid and anthranilic acid, a distinct leading zone of copper ions was detectable with dithio-oxamide. Similarly, ferric iron plus triethanolamine plus either α- or β-alanine yielded a precipitate with a long leading anionic zone detectable with hydrogen sulfide (Table V). Indeed, in many experiments in which most of the ferric ions remained near the starting position, a very dilute zone of these ions may have contaminated the other cations. These observations are analogous to results obtained by washing a precipitated organic pigment in an adsorption column with fresh solvent (*13*, *14*). They show that slowly migrating zones may be contaminated with traces of the ions migrating from a precipitate.

ELECTRO-OSMOSIS AND HEATING EFFECTS

In some experiments a small migration (electro-osmosis) of solvent was observed as has already been reported during electrochromatography in columns of siliceous earth (*16*). This did not affect the relative migration rates or the separability of the ions during the short time required for the separations.

Owing to the electrical resistance of the ammonia and of the organic acids in the polyphase systems, appreciable but uniform heating of the solutions often resulted from passage of the electrical current. With dilute solutions of very strong acids, most of the heating occurred at the cathode. With dilute solutions of strong bases, most of the heating occurred at the anode. Both these effects are ascribable to the migration of the anions or cations of the electrolyte away from the cathode or anode, respectively, with resultant increase in the resistance of these regions.

SEPARATIONS

Silver group cations (about 0.005 M) were separated by one-way electrophoresis in 0.1 M lactic acid, the sequence being silver, lead, mercurous, mercuric ions, with silver migrating fastest. With acetic acid or tartaric acid as solvent, separation of mercurous from mercuric ions was not so complete as with lactic acid. Upon transverse electrolysis in the presence of ammonia plus lactic acid, the sequence was silver and mercuric ions, lead being precipitated and mercurous ions yielding mercury and mercuric ions. Bismuth ions, if present in the mixture, remained with the mercuric ions during electrophoresis in lactic acid, and they remained fixed as an insoluble product in the presence of ammonia.

With a saturated solution of versene in water, silver ions migrated to the cathode, mercuric and lead ions to the anode. In water saturated with trimethylamine-α,α',α''-tricarboxylic acid, silver ions migrated to the cathode, lead and mercuric ions to the anode, and mercurous ions formed a very insoluble precipitate. Ammonia did not alter this effect. The action of some complex-forming reagents on the migration of silver is summarized in Table V.

Table IV. Relative Chromatographic and Electrochromatographic Migration of Copper and Nickel Ions (Approximately 0.01 M) in Various Solvents

Solvent	Chromatography		Electrochromatography	
	Faster	Slower	Faster	Slower
Ammonia (4 M)	Ni	Cu	Ni to −	Cu to −
Lactic acid (0.1 M)	Ni + Cu (weak ads.)	. . .	Ni to −	Cu to −
Triethanolamine (2%)	Cu	Ni	. . .	Ni + Cu to −
Triethanolamine (2%) plus ammonia (4 M)	Cu	Ni	Ni to −	Cu to −
Triethanolamine (0.2 M) plus triethylamine (0.2 M)	Cu	Ni	Ni to −	Cu to +
Triethanolamine (0.2 M) plus NaOH (0.05%)	Cu	Ni	Ni to −	Cu to +
NaOH (0.05%)	Ni + Cu (ppt.)	. . .	. . .	Ni + Cu (ppt.)
$N(CH_2COOH)_3$ (satd.)	Ni + Cu (weak ads.)	. . .	Ni + Cu to +	. . .
Ammonia (4 M) in $N(CH_2COOH)_3$ (satd.)	Ni + Cu (weak ads.)	. . .	Ni to +	Cu to +
Triethylamine (2%) plus tartaric acid (1.5%)	Ni + Cu (weak ads.)	. . .	Cu to +	Ni to +
Tartaric acid (1.5%)	Ni + Cu (weak ads.)	. . .	Ni to −	Cu to −

Table V. Migration of Ions in Presence of Various Solvents and Complex-Forming Reagents

Solution	Sequence from Original Position (:), Negative (:) Positive
Ammonia (4 M)	Ag, Ni, Cu + Co, Fe (pptd.):
Ammonia (4 M) plus lactic acid (0.1 M)	Ag, Ni, Cu, Co, Fe:
Lactic acid (0.1 M)	Ag, Ni + Co, Cu, Fe:
Ammonia to 4 M in anthranilic acid (satd.)	Ag, Ni, Cu, Co, Fe:
Anthranilic acid (satd.)	Ag, Ni + Co, Cu + Fe:
Ammonia to 4 M in $N(CH_2COOH)_3$ (satd.)	Ag, Fe:Cu, Co + Ni
$N(CH_2COOH)_3$ (satd.)	Ag, Co + Fe:Cu + Ni
Ammonia (4 M) plus L(+) glutamic acid (2%)	Ag, Ni + Co + Cu + Fe:
L(+) glutamic acid (0.7%)	Ag, Ni + Co, Cu, Fe:
Ammonia (4 M) plus triethanolamine (2%)	Ag, Ni, Cu, Fe:Co
Triethanolamine (2%)	Ag + Ni + Cu, Co + Fe:
Triethanolamine (2%) plus lactic acid (0.1 M)	Ag, Ni, Co, Cu, Fe:
Triethanolamine (0.2 M) plus triethylamine (0.2 M)	Ag, Ni, Fe:Cu, Co
Triethanolamine (2%) plus DL-α-alanine (2%)	Cu:Fe (pptd.), Co + Ni + Ag + Fe
Triethanolamine (2%) plus β-alanine (2%)	Co + Ni + Cu:Fe (pptd.), Co + Ag + Fe
Triethylamine (2%)	Ag + Ni + Co + Cu + Fe:(all pptd.)
Triethylamine (2%) plus urea (2%)	Ag + Ni + Co + Cu + Fe:(all pptd.)
Triethylamine (2%) plus L(+) glutamic acid (2%)	Ag, Fe:Cu + Co + Ni
Triethylamine (2%) plus DL-α-alanine (2%)	:Fe (pptd.) Cu, Co + Ni + Ag
Triethylamine (2%) plus β-alanine (2%)	:Fe + Co (pptd.) Cu, Co + Ni + Ag
Triethylamine (2%) plus tartaric acid (1.5%)	Ag:Co, Ni, Cu, Fe
Tartaric acid (1.5%)	Ag, Co + Ni, Cu, Fe:
DL-histidine monohydrochloride (1%)	Ni + Co + Cu, Ag + Fe:
Potassium cyanide (0.4%)	:Fe, Ag, Cu + Ni

Copper group cations were separated by one-way and two-way electromigration as indicated by Figure 2. Silver, with a higher migration rate than any of these cations, was separated from them rapidly and completely in either acidic or ammoniacal solutions (Table V).

Tin group cations, stabilized in 0.2 M tartaric acid, were separated by one-way electromigration in 0.1 M lactic acid wherein stannous ions migrated to the cathode, arsenious ions did not migrate, and antimonious ions migrated to the anode. In 0.05 M tartaric acid, in 0.05 M tartaric acid plus 0.1 M lactic acid, and in saturated trimethylamine-α,α',α''-tricarboxylic acid, both stannous and antimonious ions migrated to the anode, while arsenious ions remained neutral. Addition of a solution of the ions in strong hydrochloric acid to a paper saturated with 0.1 M lactic acid resulted in a very slow and incomplete separation by electrolysis.

Iron and aluminum group cations were separated by two-way and by three-way electrical migration. In 0.1 M lactic acid, chromic ions migrated rapidly to the cathode; aluminum ions migrated more slowly; ferric ions did not migrate; and chromate ions migrated rapidly to the anode, so that these four ions were separated by a one-way development. Under these conditions manganous, cobalt, nickel, and zinc ions migrated with the chromic ions. If the chromic ions were oxidized to chromate before the one-way development in acid, a succeeding two-way development in ammoniacal solution separated most of the elements of this group. Manganese remained in an insoluble form; cobalt oxidized to a cationic form and migrated slowly from manganese; and nickel plus zinc migrated away from the cobalt ions, the nickel moving slightly faster than the zinc. With ammonia plus 2% triethanolamine as electrolyte, zinc migrated slower than nickel, and cobalt migrated slightly toward the anode. Use of this solvent for three-way development of a strip cut from the two-way chromatogram improved the separation of cobalt, manganese, zinc, and nickel.

Subgroups of the iron and aluminum family were readily separable by one-way electrolysis. In addition to the separation of ferric, aluminum, chromic, and chromate ions, ferric and manganous ions and aluminum, zinc, and chromate ions were also separated in lactic acid. Aluminum, zinc, and chromate ions were separated in lactic acid, in 2% triethanolamine plus 4 *M* ammonia, and in 4 *M* ammonia. In triethanolamine (2%) plus triethylamine (2%) both aluminum and zinc were weakly anionic. Cobalt and nickel were separated in 4 *M* ammonia, in 4 *M* ammonia plus 2% triethanolamine, and in triethanolamine (2%) plus triethylamine (2%) (Table V).

Ions of several groups exhibited the electrical migration behavior summarized in Table V. In the presence of complex-forming agents, many cations exhibited anionic properties, and with different reagents, various ions of the mixtures could be made the leading electrochromatographic zones. These results indicate that various solvents may be utilized to effect a complete separation of particular components from mixtures. Thus with triethanolamine plus triethylamine, copper and cobalt may be separated completely from nickel or silver; with trimethylamine-α,α',α''-tricarboxylic acid, copper and nickel may be separated completely from cobalt and silver; with ammonia plus triethanolamine, cobalt may be separated completely from copper, nickel, and silver; with triethanolamine plus glutamic acid, copper, cobalt, and nickel may be prepared free of silver. As each ion formed a single zone during electromigration, the complexes with organic solutes must have been in dynamic equilibrium.

Mixtures of various organic compounds were readily separated by one-way and by two-way electrolysis. In 4 *M* ammonia, pyrogallol migrated to the anode and separated from neutral glucose and sucrose, and weak bases such as triethanolamine separated rapidly from acidic substances such as anthranilic, arsanilic, salicylic, and sulfanilic acid. In 0.1 *M* acetic acid solution, anthranilic acid migrated to the cathode and separated from salicylic acid, which migrated rapidly to the anode, and from *p*-arsanilic acid, which migrated slowly to the anode. By one-way development in 0.1 *M* acetic acid, sulfanilic acid migrated rapidly to the anode and separated from arsanilic acid, which remained with neutral surcrose. In succeeding two-way development in the presence of ammonia, the arsanilic acid migrated rapidly to the anode and separated from the neutral sucrose.

SUMMARY

Two-way and three-way electrolytic development extend the scope of chromatographic methods. Variation of solvent, with concomitant variation of adsorbability, absorption sequence (*15*), and ionic mobility, facilitates the resolution of mixtures and the isolation and identification of the components. Accordingly, two-way and three-way electromigration in polyphase systems must be regarded as extremely sensitive and widely applicable analytical tools.

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Analysis of Mixtures of Carboxylic Acids

By Spectrophotometric Determination of Rate of Reaction with Diphenyldiazomethane

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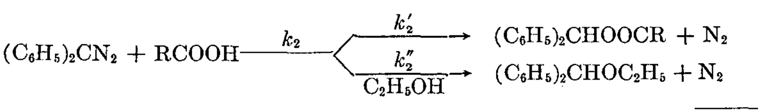
IN THE course of investigations (*2–4*) of the reactions of diazo compounds with various types of acids, the authors have had occasion to develop methods for analysis of mixtures of carboxylic acids by measurement of their reaction rates with diphenyldiazomethane. The carboxylic acid–diphenyldiazomethane reaction has obvious advantages for this purpose, as it is very convenient to follow spectrophotometrically (the diazo compound has a deep permanganatelike color), occurs in a wide range of solvents, and may be carried out with small amounts of materials. Furthermore, different carboxylic acids often show substantial differences in rate—for example, *p*-nitrobenzoic acid reacts approximately 25 times faster than *p*-aminobenzoic acid in ethyl alcohol at 30°. The principal disadvantages of the reaction for analytical purposes are the lack of simple stoichiometry in solvents like ethyl alcohol, where the reaction rate is strictly second-order, and nonintegral kinetic orders in carboxylic acid in aprotic solvents, where the reaction is quantitative. It is the purpose of the present paper to show how these disadvantages may be overcome in the analysis of binary acid mixtures.

Detailed procedures for the spectrophotometric determination of the reaction rate of diphenyldiazomethane with acids using a Beckman DU spectrophotometer with a thermostated cell compartment have been published (*1–4*).

In ethyl alcohol, the instantaneous rate of the reaction between carboxylic acids and diphenyldiazomethane is strictly proportional to the first powers of the acid and diazo compound concentrations. However, the acid not only reacts directly to yield the corresponding benzhydryl ester but also catalyzes the forma-

Procedures have been developed for the analysis of carboxylic acid mixtures by spectrophotometric determination of reaction rate with diphenyldiazomethane in alcohol or benzene solution. The median deviations in about 25 determinations of different types including mixtures of acetic and benzoic acids, *m*- and *p*-methoxybenzoic acids, and acetic and chloroacetic acids were about 2%.

tion of benzhydryl ethyl ether through reaction of diphenyldiazomethane with ethyl alcohol (*3*). As a consequence, the rate does not follow the simple integrated second-order rate equation at comparable acid and diphenyldiazomethane concentrations (*3*)



$$(C_6H_5)_2CN_2 + RCOOH \xrightarrow{k_2} \begin{cases} \xrightarrow{k_2'} (C_6H_5)_2CHOOCR + N_2 \\ \xrightarrow[C_2H_5OH]{k_2''} (C_6H_5)_2CHOC_2H_5 + N_2 \end{cases}$$

and determination of the composition of an acid mixture by analyzing the form of the reaction rate curve would be a complex task under such conditions. A simple procedure in this situation, which is applicable to binary mixtures (A, B) is to use a several-fold excess of acid over diphenyldiazomethane and determine the pseudo-unimolecular rate constant k_1 for the disappearance of diphenyldiazomethane. The composition may then be obtained in the following way if A and B are in large excess.

$$k_1 = k_{2_A}[A] + k_{2_B}[B]$$

$$k_1/([A] + [B]) = k_{2_A}[A]/([A] + [B]) + k_{2_B}[B]/([A] + [B])$$

$$X_B = 1 - X_A$$

$$X_A = [A]/([A] + [B]) = (k_2 - k_{2_B})/(k_{2_A} - k_{2B}) \qquad (1)$$

where k_{2_A} and k_{2_B} = the separately determined rate constants for the pure acids A and B; [A] and [B] = the concentrations of A and B in the rate run solutions; and X_A and X_B = mole fractions of A and B in acid mixture

This method has been applied to the analysis of mixtures of acetic and benzoic acids as well as of *m*- and *p*-methoxybenzoic acids. With each of these pairs, the ratio of k_{2A} to k_{2B} is less than a factor of 2 and k_1 must be determined with considerable care for satisfactory analyses. Comparisons of calculated and found values for a number of acid mixtures are given in Table I. The median deviations were about 2%.

In aprotic solvents, such as benzene, the reactions between carboxylic acids and diphenyldiazomethane appear to yield benzhydryl esters quantitatively and it is possible to determine carboxylic acids by colorimetric estimation of total diazo compound consumption. Rate studies are complicated by the fact that, although the kinetic order with respect to diphenyldiazomethane is exactly first-order, the order with respect to carboxylic acids is not exactly integral in benzene, chloroform, ethylene dichloride, acetonitrile, and acetone (cf. data for benzene in Table II), presumably because of association between the acid molecules. As a result, determination of acid mixtures by rigorous mathematical analysis of rate curves in aprotic solvents is an almost impossible undertaking. However, it is possible to estimate colorimetrically a rather reactive acid in the presence of a relatively large amount of a less reactive acid (or acids) by making appropriate corrections for the diphenyldiazomethane consumed by the less reactive acid.

Table II. Variation of Rate Constants with Acid Concentration for Reactions of Carboxylic Acids with Diphenyldiazomethane in Benzene at 30.0° C.

Acid	Concn., Mole/L.	k_2, Mole^{-1} L. Min.$^{-1}$
CH_3COOH	0.0514	0.513
	0.0771	0.555
	0.1027	0.598
$ClCH_2COOH$	0.00162	0.105
	0.00323	0.175

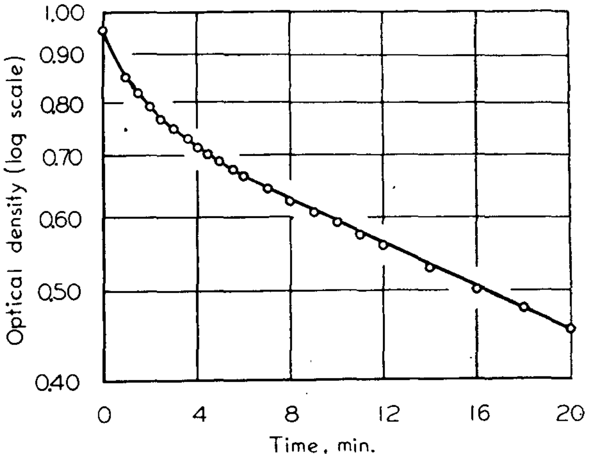


Figure 1. Rate Curve for Reaction of Diphenyldiazomethane with Mixture of Chloroacetic and Acetic Acids in Benzene at 30° C.

Table I. Analysis of Carboxylic Acid Mixtures by Rate of Reaction with Diphenyldiazomethane in Absolute Ethyl Alcohol at 30.0° C.

Acetic Acid–Benzoic Acid Mixtures

Total acid concn., mole/l.	Half time of reaction, min.	$k_1/([A] + [B])$, moles^{-1} l. min.$^{-1}$	% Acetic Acid in Mixture	
			Calcd.	Found
0.0767	8.8	1.030	0.0	..
0.1278	5.9	0.919	20.0	25.1
0.1022	7.3	0.929	25.0	22.8
0.0767	9.95	0.908	33.3	27.6
0.1278	6.35	0.854	40.0	39.7
0.1022	8.38	0.809	50.0	49.9
0.0767	11.84	0.763	66.7	60.3
0.1022	9.66	0.702	75.0	74.0
0.1278	7.9	0.686	70.0	77.6
0.0767	15.4	0.587	100.0	..

m- and *p*-Methoxybenzoic Acid Mixtures

Total acid concn., mole/l.	Half time of reaction, min.	$k_1/([A] + [B])$, moles^{-1} l. min.$^{-1}$	% *m*-Methoxybenzoic Acid in Mixture	
			Calcd.	Found
..	..	0.646[a]	0.0	..
0.1364	6.95	0.731	16.7	17.4
0.1137	8.45	0.721	20.0	15.3
0.0910	9.8	0.777	25.0	26.8
0.0682	12.55	0.809	33.3	33.3
0.1137	7.18	0.849	40.0	41.5
0.0910	8.75	0.871	50.0	46.0
0.1137	6.55	0.930	60.0	58.1
0.0682	10.15	1.001	66.7	72.6
0.0910	7.58	1.005	75.0	73.4
0.1137	5.83	1.045	80.0	78.4
0.1364	4.95	1.026	83.3	77.7
0.0455	13.42	1.135	100.0	..

[a] Average of five runs using different concentrations.

The procedure is well illustrated by determination of chloroacetic acid in acetic acid, where the k_2 values differ by a factor of 100 in benzene.

A typical rate curve for a 1 to 16 chloroacetic-acetic acid mixture is shown in Figure 1. Here, the initial rapid reaction with chloroacetic acid is essentially complete in 8 minutes and the balance of the reaction displays the pseudo-unimolecular kinetics expected for the excess acetic acid. The total acid consumption in the first 8 minutes is easily determined colorimetrically and the major problem is to compute the amount consumed by each component of the acid mixture.

Letting [DDM] represent the diphenyldiazomethane concentration and taking A and B as acetic and chloroacetic acids, respectively, the differential form of the rate equation in the first 8 minutes is

$$-\frac{d[\mathrm{DDM}]}{dt} = -\frac{d[\mathrm{A}]}{dt} - \frac{d[\mathrm{B}]}{dt} = [\mathrm{DDM}]\left[f_{\mathrm{A}}([\mathrm{A}])\right] + [\mathrm{DDM}]\left[f_{\mathrm{B}}([\mathrm{B}])\right] \quad (2)$$

where $f_A([A])$ and $f_B([B])$ are unknown functions which depend on the respective concentrations of A and B and symbolize the fact that the kinetic orders are not exactly integral in the acid concentrations.

Because acetic acid is present in large excess, its concentration does not change appreciably throughout the rate run and, consequently, $f_A([A])$ is constant and equal to the pseudo-unimolecular rate constant k_{1_A} obtained from the rate curve (*1*) after 8 minutes, if the reasonable assumption is made that chloroacetic acid does not catalyze or inhibit the reaction between acetic acid and the diazo compound. During the first 8 minutes, the consumption of of diphenyldiazomethane by acetic acid is given by the expression

$$-\int_{[\mathrm{A}]_0}^{[\mathrm{A}]_8} d[\mathrm{A}] = \int_0^8 [\mathrm{DDM}]\left[f_{\mathrm{A}}([\mathrm{A}])\right] dt = \int_0^8 k_{1_\mathrm{A}}[\mathrm{DDM}]dt \quad (3)$$

The complex kinetics of the chloroacetic acid reaction (when the acid concentration changes markedly) prevent mathematical evaluation of [DDM] and integration of Equation 3. However, graphical integration may be used, since instantaneous [DDM] values can be obtained from the rate curve. Such graphical integration was carried out by multiplication of k_{1_A}, obtained from the slope of the rate curve after 8 minutes, by the observed concentrations of the diazo compound at 0.25-minute intervals over the first 8 minutes to give a set of instantaneous acetic acid--diphenyldiazomethane reaction rates. The diazo compound concentrations were computed from the optical density readings and the separately determined molal extinction coefficient (ϵ = 103) at 525 mμ in benzene. The instantaneous reaction rates were plotted against time and integrated graphically from 0 to 8 minutes. The chloroacetic acid concentration was then obtained as the difference between the calculated initial diphenyldiazomethane concentration and the sum of the concentration at 8 minutes, and the concentration change corresponding to the acetic acid reaction in the first 8 minutes as obtained from the graphical integration.

Table III. Determination of Chloroacetic Acid in Mixtures with Acetic Acid by Reaction with Diphenyldiazomethane in Benzene at 30.0° C.

Total HOAc Concn.	Time, t, Min.[a]	$[\mathrm{DDM}]_0^b$	$[\mathrm{DDM}]_t^c$	[DDM] HOAc[d]	Weight % $ClCH_2CO_2H$ in Acid Mixture Calcd.	Weight % $ClCH_2CO_2H$ in Acid Mixture Found
0.0514	8	0.00927	0.00624	0.00138	4.7	4.8
0.0514	9	0.00927	0.00451	0.00152	9.0	9.0
0.0514	9	0.00920	0.00428	0.00150	9.0	9.5
0.0514	9.5	0.00898	0.00432	0.00157	9.0	8.6
0.0257	14	0.00971	0.00390	0.00095	22.9	22.9

[a] Time required for essentially all chloroacetic acid to react.
[b] Initial diphenyldiazomethane concentration, mole/l.
[c] Diphenyldiazomethane concentration at time t, mole/l.
[d] Diphenyldiazomethane calculated to have been consumed by acetic acid up to time t, mole/l.

The results of five runs of this type using several chloroacetic acid concentrations are summarized in Table III. The agreement between calculated and found is generally good, with a median accuracy of about 2%, despite the rapidity of the initial reaction.

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Determination of Carbon, Oxygen, and Sulfur in Copper

Vacuum Fusion Analysis Using the Mass Spectrometer

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THE vacuum fusion method of analysis has been used extensively by the steel industry for a number of years. Murray and Ashley (*7*) and Nesbitt and Henderson (*8*) are among those describing methods for carbon determination in steel. Included in the many reports on oxygen determination are Vacher and Jordan (*9*), McGeary, Stanley, and Yensen (*6*), and Alexander, Murray, and Ashley (*1*). In vacuum fusion analysis the system generally consists of a furnace chamber for conveying the element sought into a particular gas and an analytical system for obtaining pressure-volume measurements on the desired gaseous constituent. These systems necessitate the transfer of a small quantity of gas through a lengthy path, and separation by either condensation or chemical absorption.

The mass spectrometer can be used to eliminate the analytical system in the conventional vacuum fusion apparatus. Use of this instrument for gas analysis has been described by Hipple (*5*), Brewer and Dibeler (*4*), and Washburn, Wiley, and Rock (*10*). In analyzing a gaseous sample with this instrument, the partial pressure of each constituent is determined independent of the total pressure. This condition is maintained in most analytical mass spectrometers over a useful pressure range of 1000. Throughout this range measurable ion currents are obtained which are a linear function of the pressure of the constituent being sought. This instrument is calibrated at a known pressure with pure samples of the gases obtained in the vacuum fusion process. Partial pressures of the desired constituents in the unknown sample can be readily determined. The mass spectrometer is extremely useful not only in making the analyses, but also in following the development of a suitable vacuum fusion method. It not only yields a measure of the quantity of gas, but at the same time permits positive identification of the molecular mass.

The mass spectrometer pumping system was used to evacuate the furnace. This reduced the construction of the vacuum fusion apparatus to that of a furnace chamber and minor glass connec-

This work was undertaken to develop simple and rapid quantitative methods of determining carbon, oxygen, and sulfur in copper in concentrations as low as 0.0001 weight %. Rapid vacuum fusion methods for determining carbon and sulfur in copper in the range 0.0050 to 0.0001 weight % were developed using the mass spectrometer. A simple system for determinining oxygen in copper in the range 0.04 to 0.02 weight % was disclosed. Little difficulty is seen in extending this determination to 0.0001 % with the suggested refinements. The mass spectrometer serves to replace the analytical train associated with the conventional vacuum fusion apparatus. It not only provides more rapid gas analyses, but also enables positive identification of molecular structure. Its sensitivity surpasses the conventional vacuum fusion apparatus and thus provides a means for extending this method of analysis to lower concentrations.

tions. The attachment of the vacuum fusion apparatus directly to the mass spectrometer eliminated the transfer of the gaseous sample to a separate container, thus avoiding extensive delay between time of collecting sample and making the analysis. This technique minimizes absorption and contamination risks.

CARBON DETERMINATION

The furnace system employed for the determination of carbon in copper was similar to that described by Bever and Floe (*3*). The determination of the carbon content involved the transformation of the carbon into carbon dioxide, measurement of the pressure and volume of the gas obtained, and calculation of the weight percentage of carbon using the known weights of the copper samples.

A schematic diagram of the system used, excluding the mass spectrometer is shown in Figure 1.

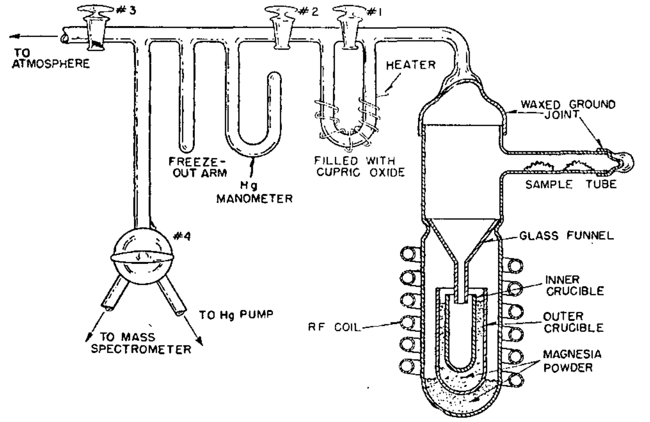

Figure 1. System for Carbon Determination

The outer Alundum crucible was 3.5 inches long and 1.25 inches in diameter with a wall thickness of 0.125 inch. The inner Alundum crucible was 3.25 inches long and 0.625 inch in diameter with a 0.60-inch wall. Magnesia powder was used as a packing material between the crucibles and for insulating the outer crucible from the borosilicate glass envelope. At the start of each run the inner crucible contained 10 to 20 grams of copper and approximately 5 grams of cupric oxide. Weighed samples to be analyzed were stored in the sample tube. These numbered not more than six and weighed approximately 10 grams each. The physical shape of the sample was found to be unimportant. Preparation of the sample included degreasing, etching in nitric acid, and rinsing in distilled water.

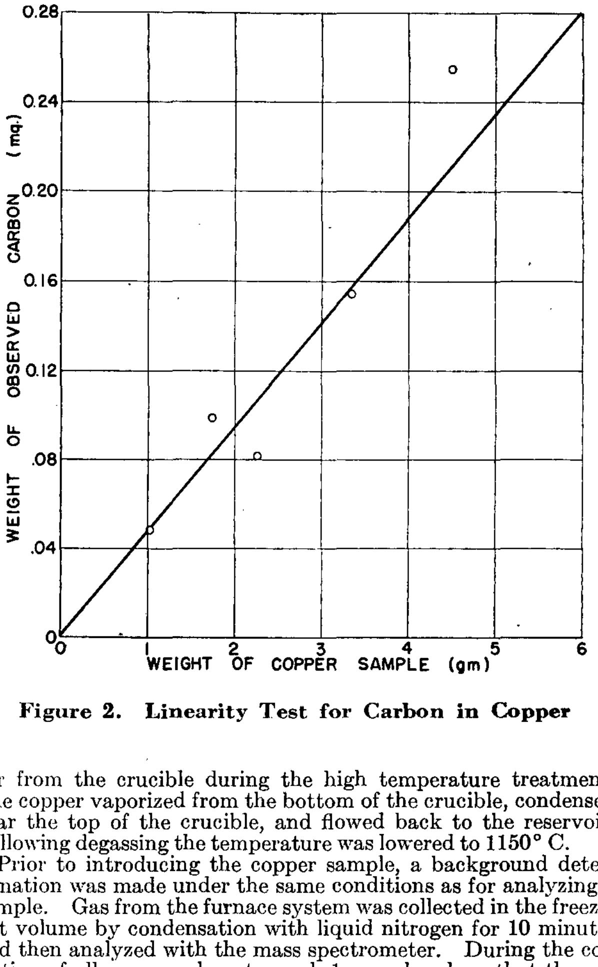

Figure 2. Linearity Test for Carbon in Copper

Initially the system was thoroughly degassed by heating the copper and copper oxide to 1300° to 1400° C. for approximately 1 hour. A thermocouple gage indicated when the degassing was completed. The low vapor pressure of copper at its melting point prevented the escape of any appreciable amount of the copper from the crucible during the high temperature treatment. The copper vaporized from the bottom of the crucible, condensed near the top of the crucible, and flowed back to the reservoir. Following degassing the temperature was lowered to 1150° C.

Prior to introducing the copper sample, a background determination was made under the same conditions as for analyzing a sample. Gas from the furnace system was collected in the freeze-out volume by condensation with liquid nitrogen for 10 minutes and then analyzed with the mass spectrometer. During the collection of all gas samples, stopcock 1 was closed, so that the gas sample passed over the cupric oxide, which converted any carbon monoxide present into carbon dioxide. The cupric oxide was maintained at 350° C. Gas collected was analyzed for water, sulfur dioxide, and carbon dioxide. The background and sample gases were high purity carbon dioxide as measured with the mass spectrometer. This is in agreement with Bever and Floe's discussion of their results. However, it was experimentally verified that sulfur dioxide was rapidly absorbed by the cupric oxide at 350° C. and that this accounts for the absence of sulfur. The mass spectrometer measurement of the carbon dioxide gave the pressure in a standard volume, which consisted of the system enclosed by stopcocks 2, 3, and 4. From the pressure, volume, and temperature of the carbon dioxide, the carbon background was determined. The carbon concentration in a weighed copper sample was evaluated in the same manner, taking into account the background correction. The background correction used was the average of that before and after treating the sample. It amounted to less than 0.000025% carbon by weight for a 10-gram sample.

Figure 2 shows the results of a linearity test made on the method. This particular copper has a high carbon content due to high temperature treatment in a graphite crucible.

Table I gives typical results for three Chilean copper samples. The average carbon content approximates 0.0001 weight %. This figure agrees with the solubility data of Bever and Floe for the refining temperature, which is in the neighborhood of 1100° C.

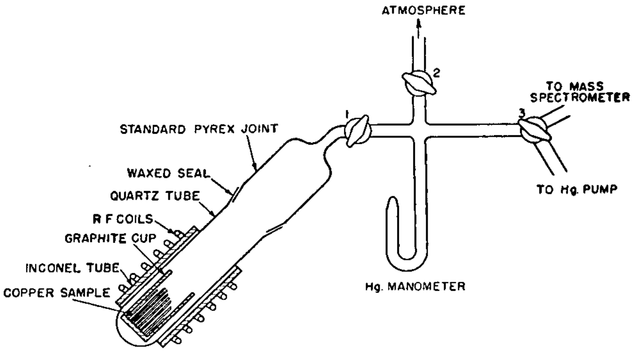

Figure 3. System for Oxygen Determination

A second method of determining carbon in copper, which required complete oxidation of the copper at approximately 1600° C., was tried and discarded. The carbon results were erratic and higher than those obtained by the described method. It is believed this method fails because of reaction of the molten copper oxide with the refractory retaining crucible. The crucible is a source of carbon in addition to the copper sample.

OXYGEN DETERMINATION

Sample weight and preparation for the oxygen determination were the same as for the carbon analysis. The system shown in Figure 3 was used for the oxygen determination.

Table I. Carbon Content of Three Chilean Copper Samples

Sample No.	Carbon by Weight, P.P.M.
1	1.3 1.0
2	1.1 0.8
3	0.7 1.0

Prior to making any determinations the quartz tube and carbon crucible were degassed at 1200° C. for 15 to 20 minutes. The power was then shut off from the oscillator and the Inconel tube removed. After the system had cooled for 2 to 3 minutes, tank helium was admitted to the furnace at atmospheric pressure. This hastened the cooling in the absence of oxygen. When the system had cooled to near room temperature, heat was applied to the waxed joint and the quartz tube was freed. The carbon cup was removed, the weighed sample placed in it, and the system reassembled in as short a time as possible. The furnace was then evacuated as indicated by a thermocouple gage, followed by closing stopcock 1. The sample temperature was raised to 1150° C. for 10 minutes. Deoxidation of the copper by carbon and carbon monoxide was completed in this time, as evidenced in Figure 4. Stopcock 1 was opened and the pressure read on the manometer with the furnace at 1150° C. Analysis of the sample with the mass spectrometer revealed high purity carbon monoxide. Having established this, it was then possible to eliminate the mass spectrometer, and for the high oxygen concentration being studied to use the mercury manometer for pressure measurements. The standard volume used consisted of the furnace and the manometer. Initial degassing of the furnace system was necessary only at the start of each day's work. The system permitted analysis of 15 to 20 samples per 8-hour day.

To obtain the weight percentage of oxygen in the copper by the method described, it was necessary to obtain experimentally a number of factors. The volumes of the furnace and manometer were measured by comparison to a standard volume. In order to calculate the weight of oxygen in the gas obtained, it was necessary to know the ratio of pressure in the total system at room temperature to that with the furnace at 1150° C. Measurements of this factor using argon, helium, and carbon monoxide gave the room temperature pressure as 84% of the pressure with the furnace at 1150° C. This factor was used to correct the pressure reading throughout this work. In addition, it was necessary to make a background correction for the furnace. This was due to absorbed gas on exposure of the system to atmospheric pressure when introducing the sample. A number of background runs gave this pressure correction as 1 mm. of mercury in the standard volume when measured with the same procedure as used for analyzing the sample. This background correction was made for all analyses. The pressures obtained for the typical samples analyzed were in the range 20 to 30 mm. of mercury. It is common practice in vacuum work to admit an inert atmosphere rather than air to the system to enable faster recovery of the vacuum. The helium used gave this result and thus a more reproducible background as well as shortening the time of cooling.

The results of the described method have been compared with results obtained on a standard vacuum fusion system for steel operated at 1650° C., and a system employing conversion of the

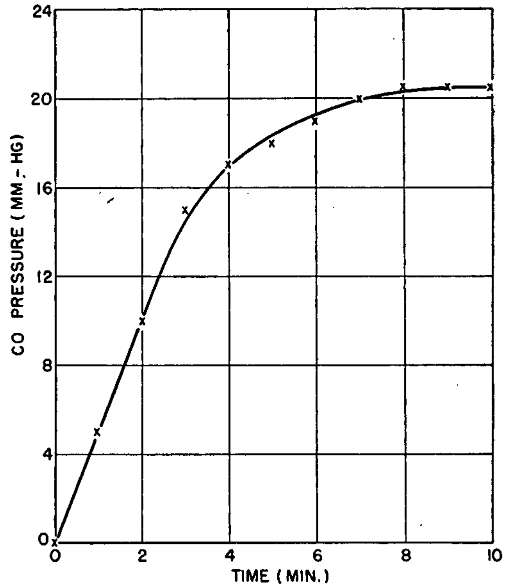

Figure 4. Carbon Monoxide Pressure from Heating of Copper in Carbon Boat at 1150° C. in Isolated System as Function of Time

Table II. Oxygen Content of Some Chilean Copper Samples

Sample No.	Oxygen, Weight %
1	0.0210 0.0215 0.0215 0.0220
2	0.0235 0.0240 0.0245 0.0240 0.0230
3	0.0260 0.0250 0.0260

oxygen into water by means of hydrogen. The results of all three methods were in good agreement. Typical results for some Chilean copper samples are shown in Table II.

It is felt that a system capable of detecting 0.0001% oxygen could be made by the addition of a few refinements. These would include a sample introduction system which would permit thorough degassing in order to reduce the background, use of the mass spectrometer for measuring the pressure of the particular gaseous constituent desired independent of other gases, and possibly conversion of the carbon monoxide into carbon dioxide as in the carbon determination to enable easy concentration of the gas into a small volume which would yield a large working pressure for the mass spectrometer.

SULFUR DETERMINATION

In the development of a method of determining sulfur in copper, a number of different techniques were tested. A method was desired that would convert the sulfur into a stable gas at room temperature in order that the mass spectrometer could be used to determine the quantity of sulfur rapidly. Hydrogen treatment of the copper above the melting point was disregarded because of the slow reaction of hydrogen with the sulfide (*2*). Vacuum melting for a reasonable length of time was found to remove only a part of the sulfur as sulfur dioxide which could be analyzed. Complete oxidation of the copper required high temperatures, a large source of high purity oxygen, and a means of handling the molten oxide. An oxidized Inconel surface could be used for holding the molten copper oxide, but in spite of decarbonization of the Inconel at 1000° C. for 16 hours in wet hydrogen, it released large quantities of carbon when in contact with the molten oxide. This plus other difficulties seen in analyzing a large number of samples by such a method caused its abandonment.

The method which was developed and used was that of converting the sulfur into sulfur dioxide. It was found that the addition of an oxide coating to the copper sample followed by heating to 1100° C. yielded recovery of the sulfur as sulfur dioxide. In Figure 5 is shown a schematic diagram of the system used.

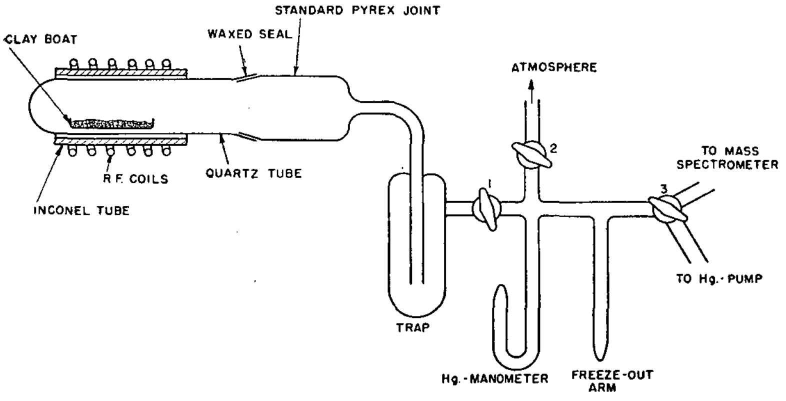

Figure 5. System for Sulfur Determination

Ten-gram samples prepared as described above were used. The clay combustion boat was degassed prior to its first usage. A weighed sample was placed in the boat and the quartz tube attached by means of the waxed joint. The system was evacuated and the *r-f* generator set into operation to yield a temperature of approximately 700° C. After the system had been degassed at this temperature as indicated by a thermocouple gage, it was isolated by stopcock 3. Approximately 15 cc. of tank oxygen were admitted through stopcock 2. Liquid nitrogen was then placed on the trap to maintain a low partial pressure of sulfur dioxide above the copper. The copper was heated to a temperature of 1100° C. for 30 minutes. The quartz tube was then cooled and the noncondensed gas exhausted from the system. The condensed gas was then transferred from the trap to the freeze-out arm using liquid nitrogen. Throughout the analyses the volume isolated by stopcocks 1, 2, and 3 was used as a standard volume.

After the gas had been transferred to the standard volume, stopcock 1 was closed and the liquid nitrogen was removed from the freeze-out arm. The partial pressure of sulfur dioxide in this standard volume was measured with the mass spectrometer and the necessary calculations were made.

The described method of removing sulfur from the copper by the addition of oxygen is similar to that used in the refinery. In refining Chilean copper, air blown through the molten copper to increase the oxide content results in the removal of the sulfur. In analyzing samples, the low partial pressure of sulfur dioxide above the copper facilitates complete removal of the sulfur. The sulfur removal is complete in that a repeat analysis at a higher temperature yields sulfur approaching the background and lower limit of sensitivity for the system, which is approximately 0.000025% sulfur for a 10-gram copper sample.

Table III. Sulfur Content of Some Chilean Coppers

Sample No.	Sulfur, P.P.M. by Weight
1	10
	12
	10
2	9
	10
3	10
	12

A number of the variables examined in analyzing copper for sulfur were found not to be critical. The quantity of oxygen was varied from 10 to 20 cc. with no effect on the results. No purification of tank oxygen was found necessary, as is required in complete combustion analysis. The temperature was relatively unimportant, so long as it was above the melting temperature of copper. The time of heat treating (30 minutes) could probably be shortened, but certainly it is sufficiently long for the concentrations encountered. The coating of copper in the quartz tube did not affect the results and the same quartz tube was used for more than a month. The clay combustion boats have an average life of about six samples. The reproducibility of the method in the range 0.0010% is of the order ±15% for the particular samples studied. The magnitude of this spread to be associated with variable sulfur content of the samples and errors of measurement is difficult to determine. Some typical results are presented in Table III.

DISCUSSION

The usefulness of the mass spectrometer in the field of vacuum fusion analysis has been shown. In the extension of this method of analysis to smaller concentrations, the mass spectrometer could be the tool for supplying analytical information. It provides one of the most sensitive means of gas detection and at the same time enables identification of the molecular mass. As ordinarily used, the mass spectrometer provides an ion current measurement for a particular mass to charge ratio that is proportional to the number of atoms or molecules of the constituent passing through a given volume per unit of time. To measure extremely small quantities of gas, it may be beneficial to provide a means of integrating this ion current. The total sample would then be pumped through the mass spectrometer and the $\int i\,dt$ would be a measure of the total quantity of the particular constituent where i is the ion current for the particular m/e value and t is the time. For calibration purposes, where normally a larger quantity of gas is used than obtained from the vacuum fusion process, this method permits extrapolation over the two variables of pressure and time rather than only pressure. The lower limit of detection of a vacuum fusion apparatus using a mass spectrometer as the analytical tool will not be determined by the sensitivity of the mass spectrometer until the present limits have been decreased by several orders of magnitude. It is to be expected that the limitations will be due to other factors than that of detecting the small quantity of gas.

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Analytical Applications of the Polarography of Molybdenum

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Previous reports on the polarographic behavior of molybdate solutions exhibit an unsatisfactory lack of agreement. Investigations by the authors have shown that the polarographic characteristics of molybdate solutions are modified by the presence of nitrate ions. The previous discrepancies may be attributed to the catalytic polarographic reduction of nitrate. In the absence of nitrate, reduction of molybdate in 0.1 *M* sulfuric acid solution occurs in three steps with half-wave potentials of +0.06, −0.29, and −0.60 volt *vs.* S.C.E. The reduction current is proportional to the molybdate concentration in the range 0.02 to 1 millimolar. Either nitrate or molybdate may be quantitatively determined by utilizing the enhancement of the reduction current at −0.75 volt *vs.* S.C.E. due to the presence of nitrate. Procedures are described for the polarographic determination of molybdate in the concentration range 4×10^{-7} to 4×10^{-4} *M* and for the determination of nitrate in the range 2×10^{-4} to 5×10^{-2} *M*. The method is particularly suitable for estimation of low concentrations of molybdate.

INVESTIGATIONS of the polarography of molybdenum in weakly acidic solutions have been reported by Uhl (*10*), Hokhshtein (*2*), and Holtje and Geyer (*3*). These authors agreed that molybdate ion is polarographically reducible only in solutions more acidic than about pH 6, though in specific details their experimental results and conclusions were not in close agreement.

During an investigation by the authors of the polarographic behavior of molybdate in acidic solutions, it was noted that the presence of nitrate led to an increase in the reduction current, which was attributed to catalytic nitrate reduction. Kolthoff, Harris, and Matsuyama (*5*) reported a similar catalytic nitrate reduction activated by uranyl ion.

The conclusions of Uhl and Hokhshtein, who used nitric acid in establishing the acidity of their molybdate solutions, are invalidated by the catalytic polarographic reduction of nitrate ion by molybdenum(III). Holtje and Geyer, who used sulfuric acid in their investigations, were able to characterize the polarographic reduction steps of molybdate and to postulate a reduction mechanism, but, unfortunately, their results were not of quantitative value, possibly because of a very rapid capillary dropping rate (13.2 drops per 10 seconds).

In this paper the characteristics of the polarographic reduction waves of acidified molybdate solutions, with or without nitrate present, are described and procedures are outlined for the polarographic determination of molybdate and nitrate.

APPARATUS

The polarographic data were obtained with a Heyrovský micropolarograph, Model X, calibrated by the method of Kolthoff and Lingane (*6*). The saturated calomel reference electrode was equipped with a potassium chloride bridge which could be immersed directly in the solution in the polarographic cell. The mercury reservoir design was that suggested by McReynolds (*7*). The capillary characteristic, $m^{2/3}t^{1/6}$, was 1.30 mg.$^{2/3}$ sec.$^{-1/2}$.

REAGENTS

The sodium molybdate was purified by the method of Yagoda and Fales (*11*). All chemicals used in the investigation were of

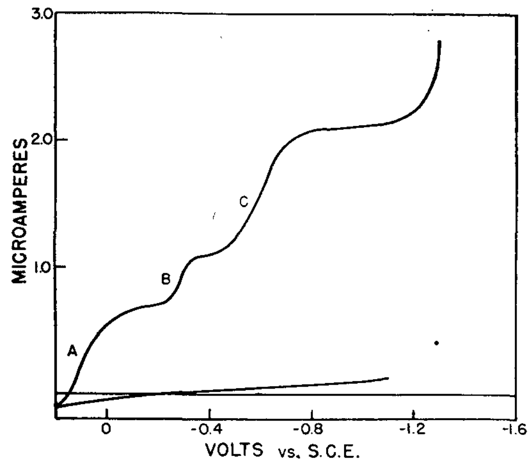

Figure 1. Typical Polarogram of Sodium Molybdate in 0.1 *M* Sulfuric Acid

8.75×10^{-5} *M* sodium molybdate, 0.1 *M* sulfuric acid, 0.2 *M* sodium sulfate reagent grade. The various solutions were prepared with distilled water.

EXPERIMENTAL

Appropriate corrections for the residual current were made for all currents reported and in calculating diffusion current constants. Potentials were referred to the saturated calomel electrode (S.C.E.). All polarographic measurements were made at 25.0° C. Oxygen dissolved in the solutions was displaced by hydrogen before polarographic measurement. Maxima suppressors were unnecessary in this investigation.

Polarographic Characteristics of Molybdate in Absence of Nitrate. Investigation of the polarography of molybdate solutions of various acidities showed that the most clearly defined wave forms were obtained in 0.1 *M* sulfuric acid containing 0.2 *M* sodium sulfate as supporting electrolyte. In Figure 1 is shown a typical polarogram of dilute molybdate in such a medium. The three polarographic waves, *A*, *B*, and *C*, represent the various reductions of molybdenum and the final rising portion of the curve represents the discharge of hydrogen.

Table I. Diffusion Current Constants of Molybdenum(VI)

(0.1 *M* sulfuric acid, 0.2 *M* sodium sulfate. $m^{2/3}t^{1/6} = 1.30$ mg.$^{2/3}$sec.$^{-1/2}$)

Molybdenum, Millimolarity	i_d, Ma.		$i_d/Cm^{2/3}t^{1/6} = K$	
	At −0.15 volt	At −0.90 volt	At −0.15 volt	at −0.90 volt
1.312	...	7.507	..	4.40
0.875	...	5.068	..	4.46
0.612	...	3.564	..	4.48
0.437	0.892	2.537	1.57	4.47
0.3500	0.720	2.037	1.58	4.48
0.2625	0.543	1.512	1.59	4.43
1.1750	0.360	1.011	1.58	4.44
0.1225	0.251	0.709	1.58	4.45
0.0875	0.179	0.499	1.57	4.39
0.0700	0.146	0.409	1.60	4.48
0.0525	0.108	0.301	1.58	4.41
0.0350	0.071	0.203	1.56	4.46
0.0175	0.036	0.104	1.58	4.57

The diffusion current for the first reduction stage is approximately one third as large as the diffusion current for the over-all reduction at each molybdate concentration. This suggests that molybdenum(VI) is reduced to molybdenum(V) at the potential of the first step and that molybdenum(III) is the product of the complete reduction. The alternative possibility of reduction to molybdenum(IV) and then to metallic molybdenum is unlikely because it conflicts with the known electrochemical characteristics of molybdate solutions.

The reduction of molybdenum(V) occurs in two unequal steps, whose combined wave heights indicate reduction to molybdenum (III). The relative magnitudes of waves *B* and *C* vary with the hydrogen ion and molybdate concentrations of the solutions. Wave *B* is proportionately greater and wave *C* correspondingly smaller in more dilute molybdate solutions or in more acidic solutions. These relationships indicate that direct reduction to molybdenum(III) occurs rather than successive reductions to molybdenum(IV) and then to molybdenum(III). Two alternative mechanisms may be suggested to explain the occurrence of two molybdenum(V) to molybdenum(III) reductions steps (waves *B* and *C*): (1) The molybdenum(V) formed by the initial reduction exists in two forms reducible at different potentials. (2) The reduction product, molybdenum(III) for each wave is different. Holtje and Geyer reported two molybdenum(III) states which required different potentials for their formation. The particular molybdenum(III) state obtained upon reduction was mainly determined by the acidity of the solution. With either interpretation only the current at the end of wave *C* represents a definite and completed valence change for the molybdenum.

Application of the equation of the reversible polarographic wave as derived by Heyrovský and Ilkovič (*1*) shows that each of the reduction waves is irreversible. The half-wave potentials for the reduction waves in 0.1 *M* sulfuric acid and 0.2 *M* sodium sulfate are, respectively: +0.06, −0.29, and −0.60 volt *vs.* S.C.E. for waves *A*, *B*, and *C*.

Determination of Molybdenum in 0.1 *M* Sulfuric Acid. The reduction currents at −0.15 volt *vs.* S.C.E., for reduction of molybdenum(VI) to molybdenum(V) and at −0.90 volt *vs.* S.C.E. for reduction of molybdenum(VI) to molybdenum(III), were found to be proportional to the concentrations of molybdate in solution and consequently suitable for establishing the concentration of molybdate. The current at −0.40 volt *vs.* S.C.E. was not suitable for measuring the molybdate concentration, as the second wave did not represent a completed valence change. The data demonstrating the proportionality of molybdate concentration to reduction current at either −0.15 or −0.90 volt *vs.* S.C.E. are shown in Table I.

Polarograms were obtained for varying concentrations of molybdate in 0.1 *M* sulfuric acid solution containing 0.2 *M* sodium sulfate. The current was determined at −0.15 and at −0.90 volt *vs.* S.C.E. and the reduction current for molybdate was calculated by subtracting the residual current values at these potentials. The diffusion current constants for molybdenum(VI) were calculated by the equation:

$$K = \frac{i_d}{C(m^{2/3}t^{1/6})}$$

where i_d is the diffusion current in microamperes, C is the molybdate concentration in millimolarity, and $m^{2/3}t^{1/6}$ is equal to 1.30 mg.$^{2/3}$ sec.$^{-1/2}$

The constancy of the ratio between the current and the concentration of molybdate indicates the validity of using the current at −0.15 or −0.90 volt *vs.* S.C.E. as a measure of the concentration of molybdate for the concentration range listed. A slight variation in the acidity of the solution or the concentration of inert salts does not affect the results. The presence of chloride ion alters the appearance of the first portion of the polarogram but does not affect the final results. Nitrate ion must be absent, as it undergoes a catalytic polarographic reduction in the presence of molybdate ion.

Substitution of the value, $K = 1.58$, from Table I for the diffusion current constant into the rearranged Ilkovič (*4*) equation, $K = 605n\sqrt{D}$, assuming $n = 1$, yields the value 0.68×10^{-5} cm.^{2} sec.$^{-1}$ for the diffusion coefficient of molybdenum(VI) in 0.1 *M* sulfuric acid.

Under the conditions described, molybdate could be determined in the range 0.02 to 0.5 millimolar at −0.15 volt *vs.* S.C.E. and 0.02 to 1 millimolar at −0.90 volt *vs.* S.C.E. The lower limit was set by the accuracy with which the limiting current and the residual current could be determined. The upper limit was set by the distortion of the curves in the more concentrated solutions. In concentrations of molybdate about 0.5 millimolar wave *A* tended to merge into wave *B*, so that there was no horizontal section of the polarogram in the neighborhood of −0.15 volt *vs.* S.C.E. In concentrations of molybdate above 1 millimolar wave *C* attained its limiting value slowly and the current at −0.90 volt *vs.* S.C.E. did not constitute the reduction of all the molybdate diffusing to the electrode.

Polarographic Characteristics of Molybdate with Nitrate Present. During investigation of the polarographic behavior of molybdate in acidic solutions, it was noted that the presence of nitrate resulted in an enhanced reduction current which was attributed to a catalytic nitrate reduction. Investigation showed that the presence of nitrate had no effect on the reduction current for the molybdate solutions until the beginning of the second wave representing the reduction of molybdenum to the trivalent state. At this and more negative potentials the reduction current was greater when nitrate was present. The results indicate that the nitrate is chemically reduced by the molybdenum(III) formed in the vicinity of the growing mercury drop. The reoxidized molybdenum is then reduced again at the cathode, resulting in an enhanced current attributable to the nitrate present. Recent experiments of Meites (*8*) show that the so-called nitrate wave in lanthanum and cerium solutions is due to the catalytic reduction of water or hydrogen ion. A similar interpretation seems unlikely in the present instance for two reasons: The reduction of water or hydrogen ion requires a higher potential than that occurring here. The effect of nitrate is the enhancement of a wave already identified with molybdate reduction.

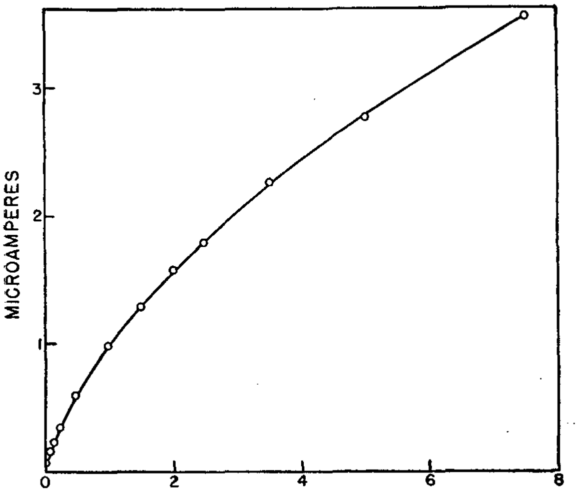

Figure 2. Calibration Curves for Nitrate in Presence of Molybdate

8.75×10^{-5} *M* sodium molybdate, 0.1 *M* sulfuric acid, 0.2 *M* sodium sulfate. Current measured at −0.75 volt *vs.* S.C.E.

Table II. Catalytic Determination of Nitrate

(0.1 *M* sulfuric acid, 0.2 *M* sodium sulfate, 8.75×10^{-5} *M* sodium molybdate. $m^{2/3}t^{1/6} = 1.30$ mg.$^{2/3}$ sec.$^{-1/2}$, residual current at −0.75 volt *vs.* S.C.E. = 0.538 μa.)

Nitrate Molarity	Reduction Current for Nitrate, μa.	$K = i/C$, μa./Molarity
1.00×10^{-4}	0.028	280
2.00×10^{-4}	0.042	210
3.00×10^{-4}	0.061	203
4.00×10^{-4}	0.080	200
5.00×10^{-4}	0.095	190
7.00×10^{-4}	0.127	181
1.000×10^{-3}	0.165	165
1.500×10^{-3}	0.235	157
2.500×10^{-3}	0.349	140
5.000×10^{-3}	0.598	120
1.000×10^{-2}	0.976	98
1.500×10^{-2}	1.29	86
2.000×10^{-2}	1.58	79
2.500×10^{-2}	1.80	72
3.500×10^{-2}	2.26	65
5.000×10^{-2}	2.76	55
7.500×10^{-2}	3.55	47

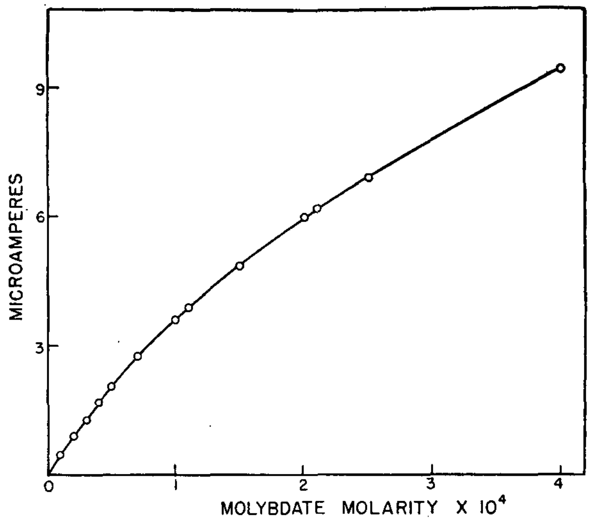

Figure 3. Calibration Curves for Molybdate in Presence of Nitrate

0.05 *M* sodium nitrate, 0.1 *M* sulfuric acid, 0.2 *M* sodium sulfate. Current measured at −0.70 volt *vs.* S.C.E.

In solutions with a low nitrate concentration, the polarograms retained the three waves characteristic of the acidic molybdate solution, wave *B* being larger than in the absence of nitrate, and waves *A* and *C* retaining the same magnitude. With a high nitrate concentration, the polarograms presented a one-wave appearance due to the magnitude of the catalytic nitrate reduction.

The nitrate diffusion current in acidic molybdate solutions may be conveniently measured at −0.75 volt *vs.* S.C.E. This is considerably less negative than the potentials of other nitrate reduction methods. With lanthanum solutions Tokuoka and Ruzicka (*9*) measured the reduction current at a potential of −1.6 *vs.* S.C.E. and with uranyl solutions Kolthoff *et al.* (*5*) used a potential of −1.2 volt *vs.* S.C.E.

Table III. Reduction Current for Molybdate Solutions in Presence of Nitrate

(0.1 *M* sulfuric acid, 0.2 *M* sodium sulfate, 0.05 *M* sodium nitrate. $m^2/^3t^1/^2 =$ 1.30 mg.$^2/^3$sec.$^{-1}/^2$, residual current at −0.70 volt *vs.* S.C.E. = 0.065 μa.)

Molybdate Molarity	Reduction Current for Molybdate, μa.	$K = i/C$, μa./Molarity ($\times 10^{-4}$)
4.00×10^{-7}	0.018	4.5
8.00×10^{-7}	0.036	4.5
1.20×10^{-6}	0.056	4.7
2.00×10^{-6}	0.091	4.6
2.80×10^{-6}	0.130	4.64
4.00×10^{-6}	0.189	4.72
6.00×10^{-6}	0.279	4.65
8.00×10^{-6}	0.376	4.70
1.000×10^{-5}	0.463	4.63
1.400×10^{-5}	0.645	4.61
2.000×10^{-5}	0.909	4.54
3.000×10^{-5}	1.292	4.31
4.000×10^{-5}	1.690	4.23
5.000×10^{-5}	2.041	4.08
7.000×10^{-5}	2.760	3.94
1.000×10^{-4}	3.63	3.63
1.100×10^{-4}	3.91	3.56
1.500×10^{-4}	4.84	3.23
2.000×10^{-4}	6.00	3.00
2.100×10^{-4}	6.23	2.95
2.500×10^{-4}	6.95	2.78
4.000×10^{-4}	9.46	2.36

Polarograms were obtained for a wide range of molybdate-nitrate concentrations in order to determine suitable conditions for the determination of nitrate and molybdate. The conditions reported in this paper were the ones finally selected for detailed study. It was found that a usable relationship could be established between the reduction current and the nitrate or the molybdate concentrations, though the relationship is not linear. From the results obtained, it appears that the reduction current for a molybdate-nitrate solution is limited not by the diffusion rates, but, rather, by the rate of chemical interaction between the nitrate and molybdenum(III). Hence calibration curves must be established to interpret the results of an analysis.

Determination of Nitrate. Polarograms were obtained for a series of sodium nitrate solutions of varying concentrations in

0.1 M sulfuric acid, 0.2 M sodium sulfate, and 8.75×10^{-5} M sodium molybdate. The nitrate reduction currents were obtained by measuring the current at −0.75 volt *vs.* S.C.E. for each nitrate concentration and from this subtracting the current at that potential for a blank solution. The results are shown in Table II.

In Figure 2 the reduction currents due to nitrate have been plotted against nitrate concentration. The relationship of reduction current to nitrate concentration is not linear, and thus it is necessary to establish a calibration curve when determining nitrate. The nitrate concentration must be 2×10^{-4} M or greater to obtain measurable current increments. The ratio of current to concentration is comparatively small, as the "diffusion" current is apparently governed by the rate of reaction between nitrate and molybdenum(III) rather than by the rate of diffusion of nitrate. Because the nitrate reduction current is not diffusion-controlled, the nitrate reduction product cannot be ascertained through application of the Ilkovič equation.

Determination of Molybdate in Presence of Nitrate. The enhanced reduction current for acidic molybdate solutions containing nitrate may be utilized to measure lower molybdate concentrations than is possible in the absence of nitrate.

Polarograms were obtained for varying concentrations of sodium molybdate in 0.1 M sulfuric acid solutions containing 0.2 M sodium sulfate and 0.05 M sodium nitrate. The reduction current was calculated by measuring the current at −0.70 volt *vs.* S.C.E. for each molybdate concentration and from this subtracting the current at that potential for a blank solution. The results are shown in Table III.

In Figure 3 the reduction currents have been plotted against molybdate concentrations. For concentrations less than 2×10^{-5} M, the reduction current is proportional to the concentration of molybdate. In more concentrated solutions the reduction current no longer increases linearly with concentration, so that a calibration curve is needed to interpret the results in this range. Molybdate solutions as dilute as 4×10^{-7} M may be estimated by this method, though obviously the accuracy is not so great when measuring diffusion current differences of this magnitude. In solutions more concentrated than those listed in Table III, the reduction step no longer exhibited a "leveling off" section in the polarogram, so that measurements in that concentration range are not recommended. By this method, molybdate in the concentration range 4×10^{-7} to 4×10^{-4} M may be determined.

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Determination of Nitrogen

Modified Kjeldahl Procedure Using Thiosalicylic Acid

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The determination of nitrogen in nitro-type compounds is a tedious operation unsuited to control operations. A simple modification of the Kjeldahl procedure permits the rapid determination of nitrogen in compounds such as nitrobenzene and nitromethane. Thiosalicylic acid is used to assist the conversion of the oxidized nitrogen to ammonia. This modification extends the scope of the method and gives greater assurance of obtaining accurate values on samples of unknown history. It is eminently suited for control operations, as some twenty determinations can be made per man-day.

THE macro-Kjeldahl procedures generally used for the determination of nitrogen in petroleum fractions do not give quantitative results with samples containing nitrogen in a higher state of oxidation, such as nitro compounds. Among the modifications that have been proposed for reducing the nitrogen to its lower valence are reduction with hydriodic acid and red phosphorus as given by Friedrich (*2*), and the procedure listed by the Association of Agricultural Chemists (*1*) using salicylic acid and sodium thiosulfate.

The micro-Kjeldahl reduction method described by Friedrich obtains good results with many compounds, but requires a considerable amount of manipulation. Each determination requires more individual attention than with the macro-Kjeldahl method and it is difficult to assure the requisite digestion temperature.

The AOAC method gives less than quantitative results with nitrobenzene and 2,4-dinitrophenol. The method gives good results with most compounds but, because of the initial reaction period prior to the addition of sodium thiosulfate and digestion, takes somewhat longer.

If the AOAC method is modified by preliminary heating with salicylic acid, followed by cooling and addition of sodium thiosulfate before continuance of digestion, results are as good as with the thiosalicylic acid method. This additional step of cooling and adding sodium thiosulfate is, however, time consuming and requires a hood, because of evolution of fumes. With this modified AOAC method, a chemist can make about 12 determinations per day.

Table I. Recovery of Nitrogen

Sample Material	Theoretical Value	Nitrogen Recovery, % by Weight: Regular Kjeldahl method 1	AOAC salicylic acid method 2	Thiosalicylic acid procedure
Nitrobenzene blended in gas oil, sample 1	0.988	0.86	0.86	0.97
			0.89	1.00
			0.92	0.95
			0.95	
			0.92	
			0.95	
			0.92	
		Av.	0.91	0.97
Nitrobenzene blended in gas oil, sample 2	0.268	0.15	0.21	0.26
		0.14	0.21	0.27
				0.26
				0.26
				0.26
	Av.	0.14	0.21	0.26
Nitroethane[a] blended in gas oil	1.04	0.95		0.99
		0.95		1.04
		0.95		
		0.95		
	Av.	0.95		1.02
2,4-Dinitrochlorobenzene[a]	13.83	0.56	12.71	13.17
		0.70	13.01	13.14
		0.51	13.23	13.33
	Av.	0.59	13.01	13.21
2,4-Dinitrobenzene propyl sulfide[a]	12.84	9.89		10.40
				10.14
				Av. 10.27
2,4-Dinitrophenol[b]	15.2	13.07	12.87	14.90
		12.66	13.34	14.70
			13.41	15.00
	Av.	13.86	13.20	14.87
Petroleum distillates[c]				
Sample 1		0.167		0.172
				0.170
Sample 2		0.033		0.032
				0.032
Sample 3		0.079		0.080
				0.080

[a] Purity unknown

[b] Eastman chemicals.

[c] Results are given on these petroleum products to show reproducibility as compared to regular Kjeldahl method on compounds of nitrogen found in petroleum.

In the course of a research investigation, two samples were submitted for routine analysis by the Bureau of Mines-Union Oil Co. of California method (*3*); one sample was 2,4-dinitrochlorobenzene, and the other was the reaction product of this compound and an amyl mercaptan.

The following results were obtained:

	Nitrogen Content as % by Weight: Theory	Analysis
2,4-Dinitrochlorobenzene, $C_6H_3Cl(NO_2)_2$	13.83	0.56
		0.70
		0.51
2,4-Dinitrobenzene amyl sulfide $C_6H_3(NO_2)_2\text{–S–}C_5H_{11}$	11.76	11.71
		9.85

These data indicated that pretreatment of nitro-type compounds was not always necessary and that the sulfur present in the molecule might be the factor affecting more complete recovery.

A limited study was made of the effect of various organic sulfur compounds on the determination of nitrogen in nitro-type compounds and petroleum fractions. In addition to thiosalicylic acid, both thio-2-naphthol and thiophenol were investigated. With nitrobenzene, thio-2-naphthol gave 95% recovery of nitrogen and thiophenol gave 100% recovery, but the latter was inconvenient to use in the laboratory because of noxious fumes.

A new procedure using thiosalicylic acid as the reducing agent has been developed. It appears to be suitable for the determination of nitrogen in nitro-type compounds and in all basic and neutral forms of nitrogen compounds found in petroleum or shale oil fractions. The procedure is simple and an operator can make some 20 determinations per day.

REAGENTS

Thiosalicylic acid. Eastman's T 2805 is suitable.

Sulfuric acid, concentrated, reagent grade.

Potassium sulfate, reagent grade.

Mercury, clean metallic.

Sodium hydroxide-sodium sulfide solution. This solution is prepared in quantity with distilled water to contain 40% sodium hydroxide and 3% sodium sulfide nonahydrate.

Boric acid solution. A 5% solution is prepared by dissolving the appropriate amount of boric acid, reagent grade, in boiling distilled water and decanting when cool from any that may crystallize out.

Standard sulfuric acid. Approximately 0.1 and 0.01 *N* solutions of sulfuric acid in distilled water are standardized to the nearest 0.0001 normality unit against a standardized aqueous sodium hydroxide solution of approximately the same normality, using methyl purple indicator. A 10-ml. buret, graduated in twentieths of a milliliter, should be used for all titrations.

Methyl purple indicator, aqueous solution, approximately 0.1% active constituent (may be purchased from Fleisner Chemical Co., Benjamin Franklin Station, Washington, D. C.).

PROCEDURE

Introduce approximately 1 gram of thiosalicylic acid into the Kjeldahl flask and add 20 ml. of concentrated sulfuric acid. Add a sample of the proper size from a weighing pipet if a volatile liquid, or by weighing in a small porcelain crucible—e.g., Coors 00000 size—if a solid or nonvolatile liquid. (While a 1-gram sample is desirable because of ease of digestion temperature control, it may vary from 0.1 to 3 grams according to expected magnitude of nitrogen content, *3*). After addition of the sample, wash down the neck of the flask with an additional 20-ml. portion of sulfuric acid. Heat until the mixture boils and spattering occurs. This gives a temperature of 274° to 288° C. Cool to room temperature and add 20 grams of potassium sulfate and 1.3 grams of clean metallic mercury. Complete as in the regular Kjeldahl with a digestion temperature of approximately 365° C. Pertinent data obtained by this procedure, compared to those obtained by the regular Kjeldahl and the AOAC methods, are shown in Table I.

CONCLUSIONS

The addition of a preheating step with thiosalicylic acid to the regular Kjeldahl procedure permits the quantitative determination of nitrogen in nitro-type compounds. The modified procedure is accurate, requires no interruption of digestion to add sodium thiosulfate for reduction, and enables a chemist to make as many as 20 determinations per day.

ACKNOWLEDGMENT

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2,9-Dimethyl-1,10-phenanthroline

New Specific in Spectrophotometric Determination of Copper

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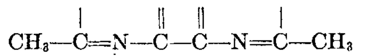
A new reagent for replacement of diquinoline as a specific reagent for determination of cuprous copper in the presence of iron is described. The procedure in the application of 2,9-dimethyl-1,10-phenanthroline involves formation of the cuprous chelate, in which 2 molecules of the substituted phenanthroline coordinate with each cuprous ion not interfered with by large amounts of iron. Its wave length of maximum absorption is at 454 mμ and the molecular extinction coefficient is 7950. The neo-cuproine–copper complex is formed over the pH range of 3 to 10 and is stable for extended periods of storage. The colored complex obeys Beer's law over the range 1 to 10 p.p.m. Neo-cuproine is soluble in alcohol and the cuprous complex may be extracted from aqueous solutions by use of amyl, isoamyl, or *n*-hexyl alcohols. No interferences from foreign ions were found. The limit of identification is 0.03 microgram of copper or 1 part of copper in 1,660,000 parts of aqueous solution after extraction with *n*-hexyl alcohol. Quantitative data are given for the determination of copper in steel.

THE use of either diethyl dithiocarbamate or dithizone in the spectrophotometric micro and macrodetermination of copper has not proved entirely satisfactory. The former is not sufficiently specific, being burdened by the reaction with the commonly present iron, nickel, and cobalt ions. The latter is likewise not satisfactorily selective in its action at a wide range of pH values, and the reagent itself is colored, requiring in its applications a mixed color procedure. For this reason Irving, Andrew, and Risdon (*5*) give a new but more complicated procedure in the the use of dithizone for the determination of copper.

A new reagent, 2,2′-diquinoline, was described by Breckenridge, Lewis, and Quick (*1*). This new copper specific was given the trivial name cuproine by Hoste (*4*), who studied the application of eight new copper specifics of the 2,2′-dipyridine type, of which 2,2′-diquinoline may be considered to be an analog, and their methyl substituted derivatives.

Hoste (*4*) designated the functional group



$$\mathrm{CH_3{-}\overset{|}{C}{=}N{-}\overset{\|}{C}{-}\overset{\|}{C}{-}N{=}\overset{|}{C}{-}CH_3}$$

as the copper specific group in 6,6′-dimethyl-2,2′-dipyridine. This reagent was sufficiently investigated to prove its superior value as a spectrophotometric reagent, but it was not seriously considered, because of difficulties in its preparation. The use of 2,2′-diquinoline serves as a practical duplicate in properties, as the two carbon atoms of the methyl groups at the two extremities of the copper specific group are incorporated into the second ring of the two quinoline molecules, giving a compound which is copper specific.

Hoste (*4*) withheld substituted types of 1,10-phenanthroline from consideration, although the unsubstituted reagent forms both ferrous and cuprous complex ions of high molecular extinction coefficients. The reason given was that these copper complexes could not be extracted from aqueous solutions by the use of known water-immiscible extraction solvents. Recent experiments in this laboratory have proved this statement incorrect.

As a result of a series of studies, such as that reported by Smith and Brandt (*6*), the compound 2,9-dimethyl-1,10-phenanthroline was at hand and known not to form the familiar red complex in the presence of ferrous iron. It was found to complex readily with cuprous copper, having the previously specified copper specific group.

The present work is a report on the further investigation of the spectrophotometric applications of this new organic compound, now given the trivial name neo-cuproine, as a superior copper specific chelating compound. Both cuproine and neo-cuproine are now commercially available (G. Frederick Smith Chemical Co.), each for the first time.

PREPARATION OF 2,9-DIMETHYL-1,10-PHENANTHROLINE

The preparation of this compound is described by Case (*2*).

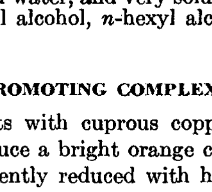
A double Skraup synthesis is employed. *o*-Nitroaniline reacts with crotonaldehyde diacetate in sulfuric acid solution; arsenic pentoxide is employed as oxidant. The 2-methyl-8-nitroquinoline thus formed is reduced to the corresponding aminoquinoline by reaction with alcoholic stannous chloride. A second Skraup reaction, duplicating the first described reaction conditions, results in the finished product in 7.6% yield based on *o*-nitroaniline. It is anhydrous when obtained from benzene extraction. It forms a hemihydrate when recrystallized from water, melting point −159° to 160° C. 2,9-Dimethyl-1,10-phenanthroline is slightly soluble in cold water, and very soluble in ethyl alcohol, *n*-amyl alcohol, isoamyl alcohol, *n*-hexyl alcohol, chloroform, and benzene.

pH RANGE PROMOTING COMPLEX FORMATION

Neo-cuproine reacts with cuprous copper in buffered acetic acid solution to produce a bright orange colored complex. The cupric ion is conveniently reduced with hydroxylamine sulfate, the excess of which need not be removed. The complex is formed over the pH range of 3 to 10. The color base material was added in the form of an alcohol-water solution, although other solvents such as amyl alcohol may be employed. The color is completely extracted by using *n*-amyl alcohol, isoamyl alcohol, or *n*-hexyl alcohol within the designated pH range. Spectrophotometric evaluation of the colored complex is conveniently performed on the extract solution.

REACTION RATIO OF NEO-CUPROINE TO CUPROUS COPPER IN COMPLEX FORMATION

The molecular ratio of neo-cuproine to monovalent copper in the orange colored complex was determined spectrophotometrically by application of the method of continuous variations and found to be 2 moles of neo-cuproine to 1 mole of copper in both water and isoamyl alcohol solutions. The complex may be formulated as:



SPECTROPHOTOMETRIC EXAMINATION OF ISOAMYL ALCOHOL SOLUTIONS OF NEO-CUPROINE CUPROUS ION

A sample of pure copper was dissolved in nitric acid and converted to sulfate by a slight excess of sulfuric acid and the desired amount of conductivity water was added. The concentration of copper was calculated to be 0.00015756 gram of copper per gram of solution. Weighed portions of the copper solution were transferred from a weight buret directly into a specially designed separatory funnel. This design was made from a standard 60-ml. borosilicate glass separatory funnel with the original stopcock replaced by a stopcock miniature of 0.5-mm. bore to provide a sharper separation of the two immiscible liquids. After the addition of excess hydroxylamine sulfate, a 100% excess of neo-cuproine in water–ethyl alcohol solution was introduced. This solution was buffered with 1 gram of sodium acetate, giving a pH between 5 and 6. The colored solution obtained was extracted with a 10-ml. portion of isoamyl alcohol. A 5-minute interval was sufficient for the separation of the two immiscible solutions. Two extractions with isoamyl alcohol were found to be adequate. The combined extracts were diluted to 50-ml. total volume with distilled isoamyl alcohol in each case. The optical density of the isoamyl alcohol solution of the complex was measured in a 1-cm. quartz cell with a Model 11 Cary recording spectrophotometer. A reagent blank correction was applied throughout.

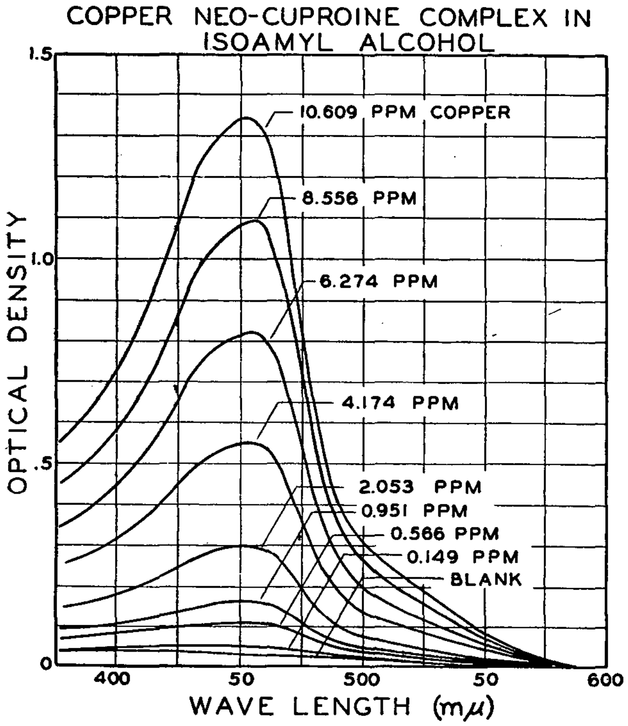


Figure 1. Copper–Neo-cuproine Complex in Isoamyl Alcohol

The results are shown in Figure 1. The data obtained are given in Table I.

APPLICABILITY OF BEER'S LAW

The data of Table I have been used in the preparation of Figure 2, which shows that Beer's law is obeyed over the range of 0.15 to 10.6 p.p.m. copper. However, other copper concentrations as high as 20 p.p.m., and as low as 0.05 p.p.m. have been successfully evaluated.

Table I. Determination of Optical Density, Wave Length of Maximum Absorption, and Molecular Extinction Coefficient of Neo-Cuproine Cuprous Ion

(Wave Length of Maximum Absorption, 454$m\mu$)

Copper Taken, Mg.	Optical Density		Molecular Extinction Coefficient
0.01491[a]	0.019		8090
0.02828	0.071		7990
0.04777	0.120		8030
0.10267	0.259		8030
0.20870	0.514		7840
0.31369	0.782		7930
0.42780	1.055		7850
0.53046	1.310		7850
		Av.	7950

[a] 100 ml. of isoamyl alcohol total volume.

STABILITY OF NEO-CUPROINE CUPROUS COMPLEX WITH TIME

A series of solutions of the type whose absorption spectra is shown in Figure 1 was prepared and measured. These solutions were stored for 17 days in clear glass in ordinary light without change in color intensity, as shown by a redetermination of the optical density. During subsequent work, low results were obtained in the quantitative determination of copper while using some undistilled isoamyl alcohol. The error was traced to oxidizing impurities in the alcohol and was removed by employing carefully redistilled alcohol in all determinations.

SPECTROPHOTOMETRIC CHARACTERISTICS OF NEO-CUPROINE CUPROUS ION

No absorption was found over the region 600 to 800 $m\mu$, but minimum absorption exists at 354 $m\mu$. The wave length of maximum absorption at 454 $m\mu$ is almost identical with the 455 $m\mu$ reported by Hoste (*4*) for the cuprous complex of 6,6′-dimethyl-2,2′-dipyridine. For the cuprous complex 1,10-phenanthroline the wave length of maximum absorption is 435 $m\mu$; this indicates an increase of approximately 20 $m\mu$ due to the presence of two methyl groups in the 2,9 positions.

The 2,9 positioned methyl groups in 1,10-phenanthroline and the corresponding 6,6′ positioned methyl groups in 2,2′-dipyridine increase in the wave length of maximum absorption of the cuprous complex to exactly the same extent when compared with the unsubstituted 1,10-phenanthroline and 2,2′-dipyridine cuprous complexes. These data are in conformity with observations of Smith and Brandt (*6*), that the methyl substitution in the 1,10-phenanthroline series of compounds has an exact numerical effect on both the wave length of maximum absorption and the oxidation potential of their ferrous complex ions.

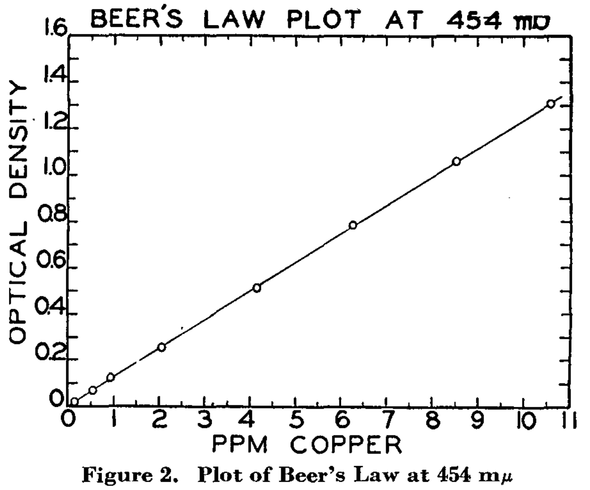


Figure 2. Plot of Beer's Law at 454 $m\mu$

The important significance of the influence of the two methyl groups of neo-cuproine is the fact that their presence renders the neo-cuproine cuprous ion completely extractable by water-immiscible alcohols at pH's below 7. Another important influence of the methyl group substitutions in neo-cuproine concerns the increase in magnitude of the molecular extinction coefficient. The value 7950 compares very favorably with that of 5490 for the 2,2′-diquinoline, 6570 for the 6,6′-dimethyl-2,2′-dipyridine, and 7040 for the 1,10-phenanthroline cuprous complexes.

SPECIFICITY

Neo-cuproine is as specific as cuproine in the presence of cations. No cation other than cuprous copper was found to form a colored

Table II. Determination of Copper in Iron with Citrate Complexing Agent

Iron Sample, Grams	Copper Added, Mg.	Copper Found, Mg.	Deviation, Mg.
1.000	0.0970	0.096	−0.001
1.000	0.0990	0.098	−0.001
1.000	0.0977	0.097	−0.000
1.000	0.0740	0.071	−0.003
1.000	0.0815	0.081	−0.000
1.000	0.1276	0.124	−0.003
1.000	0.1527	0.148	−0.004
1.000	0.1660	0.166	−0.000
1.000 (steel)	0.016[a]	0.012	−0.004
2.002 (steel)	0.032[a]	0.028	−0.004

[a] Spectrographic determination.

complex which was extractable under the conditions employed. The common anions chloride, sulfate, nitrate, perchlorate, tartrate, citrate, and acetate do not interfere. An orange-yellow precipitate occurs with large amounts of nitrate, perchlorate, and the halides (particularly iodide) upon the addition of neo-cuproine to an aqueous copper solution but causes no interference, as the colored complex is quantitatively extracted in all cases. Anions such as periodate, nitrite, thiocyanate, and ferricyanide, which either react with hydroxylamine or give a yellow colored solution, may be suitably eliminated to adapt conditions to the test. Pyrophosphate and phosphate ions do not interfere, although for excessive amounts two or three extractions may be required to collect all the copper. Neo-cuproine may thus be said to be completely specific.

LIMIT OF QUALITATIVE IDENTIFICATION

Distribution coefficient measurements on the complex obtained using *n*-amyl alcohol, isoamyl alcohol, and *n*-hexyl alcohol show that *n*-hexyl alcohol is definitely the best extraction solvent. Employing visual examination of the aqueous droplet of colored solution in a spot plate without extraction, the limit of identification is 0.04 microgram of copper. Using 1 microdrop of *n*-hexyl alcohol as extractant, the limit of identification is 0.03 microgram of copper. The limit of concentration in the former case is 1 to 1,250,000 and in the latter case 1 to 1,660,000. Therefore neo-cuproine is found to be as sensitive as dithizone (*3*).

QUANTITATIVE DETERMINATION OF COPPER IN PRESENCE OF IRON

Using citric acid as masking agent for ferric and ferrous iron at pH 4 to 6, a twofold excess of hydroxylamine hydrochloride as reductant, a 100% excess of neo-cuproine as copper reactant, and 10 ml. of *n*-hexyl alcohol as extractant, results were obtained as shown in Table II. Six grams of sodium citrate were added for each gram of iron present, but this amount is not critical.

Fluoride, pyrophosphate, oxalate, malonate, and tartrate were studied as potential masking reagents for iron in the determination, but citrate proved to be far superior within the pH range desired.

PROPOSED EXTENSION IN APPLICATION OF NEO-CUPROINE FUNCTIONAL GROUP

It has been shown that substitution of methyl groups in the 4,7-positions of the 1,10-phenanthroline molecule exerts only a small shift in the wave length of maximum absorption but a pronounced increase in the molecular extinction coefficient of the ferrous complex (*6*). Therefore it is proposed to investigate the 2,4,7,9-tetramethyl-1,10-phenanthroline derivative as a possibly improved copper specific.

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Colorimetric Determination of the Sodium Salts of Ethylenediaminetetraacetic Acid

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ETHYLENEDIAMINETETRAACETIC acid (Sequestrene) is readily determined as its alkali metal salts in the absence of alkaline earth metals and heavy metals by titration with standardized calcium acetate solution; sodium oxalate is used as an internal indicator. The end point is the appearance of permanent turbidity. In the presence of metals this method would in general determine essentially the free compound.

The alkali metal salts of ethylenediaminetetraacetic acid are widely used as alkaline earth and heavy metal sequestrants. In many cases, therefore, it is desirable to have methods of determining the total amount of the compound in very low concentrations in the presence of certain metals which may have been sequestered by it.

Nickel may be employed to displace from their ethylenediaminetetraacetic acid complexes such metals as calcium, magnesium, and many other common metals, the nickel itself being then preferentially sequestered (*6*). In a gravimetric method employing this principle (*1*) a known amount of nickel is added, and excess, unsequestered nickel is precipitated as the hydroxide and subsequently converted to the dimethylglyoxime salt for gravimetric determination. The difference, representing sequestered nickel, may be calculated to ethylenediaminetetraacetic acid, as the reaction is stoichiometric.

This gravimetric method, however, may not be sufficiently accurate when very small amounts of ethylenediaminetetraacetic acid salts are to be determined.

The method described here offers a colorimetric procedure by means of which total ethylenediaminetetraacetic acid in very low concentrations may be quantitatively determined in the presence of certain metals. Nickel is employed to displace from their Sequestrene chelates such metals as calcium and magnesium. The unsequestered nickel is removed from the sequestered nickel by a modification of the method of precipitation with dimethylglyoxime (*3*); then, as the nickel chelate is highly dissociated in strongly acid solution, it becomes possible to liberate the sequestered nickel and determine it colorimetrically in acid solution. The amount of nickel sequestered is related to the amount of ethylenediaminetetraacetic acid present. Potassium dithio-

The research was undertaken to develop a more sensitive method for the determination of small amounts of total ethylenediaminetetraacetic acid salts in the presence of calcium, magnesium, iron, and certain other metals. Commonly employed methods are not sufficiently accurate for low concentrations. In the described method, which is sensitive to 0.2 to 0.5 mg. of the compound in 100 ml. of sample solution, the test solution reacts with a nickel salt. The nickel is selectively sequestered. Excess nickel is removed with dimethylglyoxime and the sequestered nickel is liberated at low pH and determined colorimetrically as the red nickel dithio-oxalate. The intensity of the red color is related to the amount of sodium ethylenediaminetetraacetate. Because this sequestering agent is increasingly being used for water softening, for clarifying commercial soap solutions, for biochemical applications and, in general, for inactivating heavy and alkaline earth metals, a method for its determination in low concentrations in the presence of heavy metals, alkaline earth metals, and some other substances becomes of some importance. The method can be adapted to a variety of problems.

oxalate gives a bluish-red color with nickel in acid solution (*4*) and was found to be a suitable reagent for colorimetrically determining the nickel liberated from the complex.

REAGENTS AND CHEMICALS

Nickel solution, 13.3 grams of c.p. nickelous sulfate hexahydrate per liter of distilled water.
c.p. dimethylglyoxime, 1.5% in absolute ethyl alcohol.
Potassium dithio-oxalate (Eastman), 0.25% aqueous solution, freshly prepared.
c.p. aqueous ammonia, 28%.
c.p. concentrated hydrochloric acid.
c.p. calcium acetate monohydrate.
c.p. ferric ammonium sulfate dodecahydrate.
c.p. sodium acetate trihydrate.
c.p. magnesium chloride hexahydrate.
Commercially pure Sequestrene NA3 (trisodium salt, Alrose Chemical Co.).

Table I. Transmittance of Two Sets of Test Solutions

Test Solution	Mg.	Transmittance, %		Average Optical Density
Sequestrene NA3	8	36	38	0.43
	4	61	61	0.215
	1	89	89	0.05
+7 mg. of calcium	4	60	62	0.215
+12 mg. of ferric ammonium sulfate	4	60	61	0.218
+15 mg. of magnesium chloride	4	60	61	0.218

BASIS FOR THE METHOD

Experimental test solutions were prepared by diluting 8, 4, 2, 1, 0.5, and 0.0 mg. of Sequestrene NA3 to 100 ml. in each case with distilled water. Two other solutions were also prepared; one contained 8 mg. of Sequestrene NA3 and 10 mg. of calcium as calcium acetate in 100 ml. of distilled water, and the other contained 8 mg. of Sequestrene NA3 and 15 mg. of ferric ammonium sulfate in 100 ml. of distilled water. To each solution were added 15 ml. of nickel solution and 6 ml. of c.p. aqueous ammonia (28%). To these solutions, in each case, were added 15 ml. of dimethylglyoxime solution to precipitate free nickel. After 2 to 3 minutes the dimethylglyoxime nickel complex was removed by filtration, and to 50 ml. of each filtrate, 2.5 ml. of concentrated c.p. hydrochloric acid and 10 ml. of the potassium dithio-oxalate solution were added. A red to pink color resulted, depending on the amount of Sequestrene NA3 present. An 8-mg. test solution gave a red test color. A 0.5-mg. test solution showed a yellowish pink color. An 8-mg. test solution containing 10 mg. of calcium as calcium acetate or 15 mg. of ferric ammonium sulfate showed the same intensity of red color as an 8-mg. test solution without these added metals.

Testing of the filtrates (before addition of potassium dithio-oxalate) for free nickel by addition of more dimethylglyoxime showed no further precipitation of nickel.

It is therefore apparent that the sequestered nickel is not precipitated by dimethylglyoxime, and that it can be subsequently liberated for colorimetric determination with potassium dithio-oxalate and thus the amount of ethylenediaminetetraacetic acid can be estimated.

These experiments indicated further that ethylenediaminetetraacetic acid may be quantitatively determined in the presence of alkaline earth metals, ferric iron, and nickel by measuring the intensity of the red color obtained in the test procedure. This may be done by comparison with suitable color standards or by colorimetric measurement. The method has been adapted to both procedures.

SENSITIVITY

The test color results indicate that the method will detect 0.5 mg. (or less) of ethylenediaminetetraacetic acid in 100 ml. of test solution.

SPECTROPHOTOMETRIC MEASUREMENTS

Instrument. A Beckman Model B spectrophotometer employing 1-cm. matched methacrylate plastic cells was the test instrument. Hydrion short range pH papers were used for pH determinations.

Spectral Transmittance of Test Color. The red color obtained under the test conditions with nickel and potassium dithio-oxalate shows maximum absorption at 508 to 510 mμ (Figure 1).

Test Solutions for Spectrophotometric Data. Solutions were

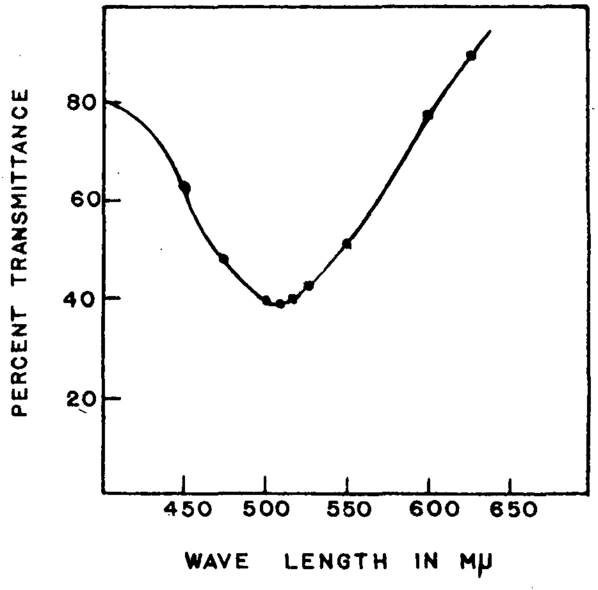

Figure 1. Absorption Spectrum of Nickel Dithio-oxalate Solution

50 ml. of distilled water, 0.0026 gram of nickelous sulfate hexahydrate, 0.7 ml. of concentrated hydrochloric acid, 10 ml. of potassium dithio-oxalate solution, 1.0 gram of sodium acetate
pH 4 to 4.5
1-cm. cell

made up to 100 ml. with distilled water containing 8, 4, 1, and 0.0 mg. of Sequestrene NA3, respectively. A 100-ml. solution containing 4 mg. of Sequestrene NA3 and 7 mg. of calcium as calcium acetate, a 100-ml. solution containing 4 mg. of Sequestrene NA3 and 12 mg. of ferric ammonium sulfate, and a 100-ml. solution containing 4 mg. of Sequestrene NA3 and 20 mg. of magnesium chloride were prepared. These test solutions were treated as described below.

The blank solution without Sequestrene NA3 was used as a reference set at 100% transmittance (O optical density). Transmittance measurements were made at 508 mμ.

Table I shows the transmittance of these test solutions and that calcium, magnesium, or ferric ions do not interfere with the determination.

Figure 2 is a plot of transmittances and Figure 3 is a plot of the optical density data shown in Table I.

INFLUENCE OF pH

Sequestering of Nickel. Experiments were run in which the nickel solution was added to the test solution before the addition of ammonia (as in the above experiments) and compared with test solutions to which ammonia was added before addition of the nickel solution.

In the absence of alkaline earth and heavy metals the same transmittance was shown in each case—i.e., adding nickel to an almost neutral solution containing ethylenediaminetetraacetic acid gave the same transmittance as that obtained by adding nickel to an ammoniacal solution. However, in the presence of calcium the displacement of the calcium and selective sequestering of the nickel occurred more completely and rapidly at initial test solution pH of 6 to 6.5 than in ammoniacal solution (Table II). Therefore, to ensure completeness of formation of nickel Sequestrene the nickel should be added to the test solution and held for 10 minutes before the addition of ammonia. Test solutions are adjusted to pH 6 to 6.5 before and not after addition of nickel solution.

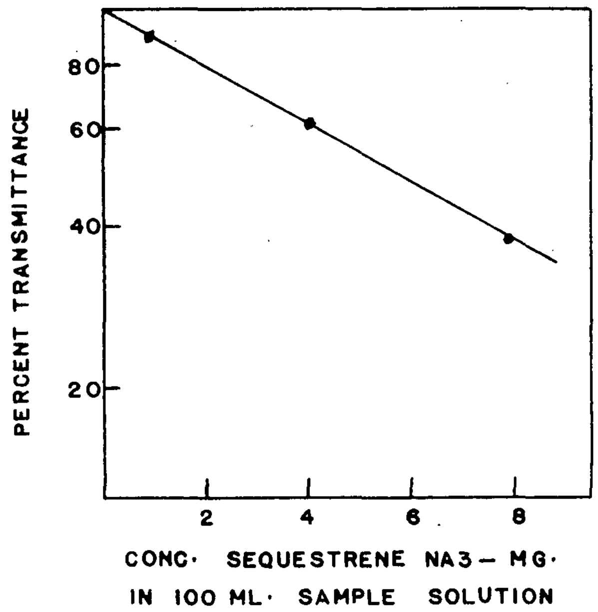

Figure 2. **Typical Transmittance Calibration Curve for Nickel Dithio-oxalate**

As measure of Sequestrene NA 3 concentration in 100 ml. of sample solution at 508 mμ in 1-cm. cells

Table II. Effect of pH on Displacement of Calcium from Sequestrene by Nickel

Test Solution	Mg.	Procedure	Transmittance, %
Sequestrene NA3	4	Nickel solution added to test solution at pH 6.5 and allowed to react 10 minutes before addition of ammonia	61
	4	Nickel solution added to ammoniacal solution and allowed to react 10 minutes	61
+ 7 mg. of calcium	4	Nickel solution added to test solution at pH 6.5 and allowed to react 10 minutes before addition of ammonia	60
+ 7 mg. of calcium	4	Nickel solution added to ammoniacal solution (pH 11) and allowed to react 10 minutes	80

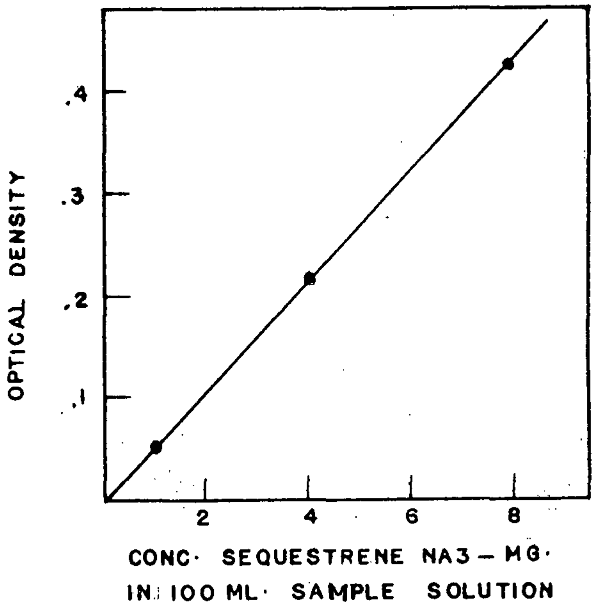

Figure 3. **Typical Optical Density Calibration Curve for Nickel Dithio-oxalate**

As measure of Sequestrene NA3 concentration in 100 ml. of sample solution at 508 mμ in 1-cm. cells

Table III. Influence of Sodium Acetate in Delaying Development of Turbidity as Shown by Transmittances

(Test solution, 8 mg. of Sequestrene NA3)

Test Solution	Transmittance, % Initial	After 10 min.	After 30 min.
Without sodium acetate, pH 1	37	26.5	21
With sodium acetate, pH 3.5–4	38–39	40	39

Liberation of Sequestered Nickel. A pH of 1 to 1.5 is necessary to liberate the sequestered nickel effectively, and the full amount (2.5 ml.) of hydrochloric acid must be used. An insufficient amount of hydrochloric acid will delay the full development of the red color. Maximum color development results when the hydrochloric acid is allowed to react with the sequestered nickel for 5 minutes before the addition of potassium dithiooxalate.

Stability of Test Solutions. The color shows adequate stability to light, although turbidity gradually develops in the colored test solutions on standing. Development of pronounced turbidity would cause errors in colorimetric or spectrophotometric measurements and in general would necessitate the preparation of a fresh test solution.

The turbidity is probably due to some decomposition of the free potassium dithio-oxalate in strongly acid solution. Weaker acids than hydrochloric acid, such as acetic acid, were tried, but they do not effectively liberate the sequestered nickel.

Table IV. Transmittances of Test Solutions Containing Sodium Acetate at pH 3.5 to 4

Test Solutions, Mg.	Transmittance, %		
	Initial	After 10 min.	After 30 min.
8	38	40	39
4	62	62	58
1	87	85	83

The development of turbidity is delayed considerably if sodium acetate is added to raise the pH to 3.5 to 4 after the nickel has been liberated and the color allowed to develop at pH 1. This is illustrated in Table III.

Table IV gives transmittances initially and after standing of 8, 4, and 1 mg. of Sequestrene NA3 test solutions adjusted to pH 3.5 to 4 with sodium acetate. It is apparent that there is ample time in which to determine transmittancy before the development of turbidity; however, the determinations should be made as soon as the test solutions are ready for measurement. In some cases it will be advantageous to prepare a calibration curve from known test solutions which have been clarified by suction filtration through asbestos after the turbidity has been allowed to develop for 30 minutes. Spectrophotometric measurements are made immediately on the filtered test solutions. The unknown in this case is likewise filtered before measurements are made. Filter paper cannot be employed, because the color is adsorbed to a great extent by the paper.

PROCEDURE

To a sample adjusted to pH 6.5 (using Hydrion short-range pH papers), and diluted to 100 ml. with distilled water at 23° to 24° C., add 15.0 ml. of nickel solution. The amount of Sequestrene present must be within the calibration range (see Figure 2). Allow the reaction to proceed for 10 minutes, then add 5 ml. of C.P. aqueous ammonia (28%). After 5 minutes add with stirring 15.5 ml. of dimethylglyoxime solution. After 5 minutes filter through No. 40 Whatman filter paper. To 50 ml. of the filtrate add 2.5 ml. of C.P. concentrated hydrochloric acid. The resulting pH should be 1. After 5 minutes add 10 ml. of freshly prepared potassium dithio-oxalate solution. After 3 to 4 minutes introduce 1.2 to 1.4 grams of solid sodium acetate crystals with stirring to give a pH of 3.5 to 4. Make the spectrophotometric measurements immediately at 508 mμ in 1-cm. cells using a blank, as reference, set at 100% *T* (O optical density). The blank consists of 100 ml. of distilled water run through the same procedure as the sample.

The graphs in Figures 2 and 3, representing typical calibration curves, are based on 100 ml. of sample solution with a blank as reference and may be used to obtain the concentration of Sequestrene in the sample.

Commercially pure Sequestrene NA3 (trisodium salt of ethylenediaminetetraacetic acid with 1 mole of water, molecular weight 376) has been used in this work. The procedure is also applicable to the determination of the mono-, di-, and tetrasodium salts. The results in terms of anhydrous Sequestrene NA3 may be converted in accordance with Table V.

Table V. Conversion Factors (for Anhydrous Compounds)

Mg. of Sequestrene NA3 × 0.8156 = mg. of ethylenediaminetetraacetic acid
Mg. of Sequestrene NA3 × 0.8770 = mg. of monosodium ethylenediaminetetraacetate
Mg. of Sequestrene NA3 × 0.9386 = mg. of disodium ethylendiaminetetraacetate
Mg. of Sequestrene NA3 × 1.0614 = mg. of tetrasodium ethylenediaminetetraacetate

Calibration curves which would pertain directly to the particular salt originally present could be prepared from knowns containing any one of the sodium salts.

It is recommended that the user prepare his own calibration curves from a series of knowns as previously described. In this way differences in equipment, technique, etc., are largely compensated for. For the most accurate results, in special cases, it might be advisable to run two or more known test solutions along with the sample and the blank.

DISCUSSION

Because this method is an empirical one, exact directions must be followed or exact proportional aliquots of all volumes used.

If it is desired to have the major portion of a calibration more closely approach a transmittancy range of 10 to 50%, a range which in a general way is considered the most reliable spectrophotometric range (*5*), graphs may be prepared from measurements in cells of greater length than 1 cm., to obtain higher absorbance.

Table VI. Reproducibility as Shown by Transmittances of Five Sets of Test Solutions

Test Solutions, Mg.	Transmittance, %				
	Set 1	Set 2	Set 3	Set 4	Set 5
8	36	37	38	38	38
4	61	60	60	61	62
1	89	89	88	88	87

Blank set at 100% transmittance.

Reproducibility. Satisfactory reproducibility of results is achieved by carefully following the analytical procedure outlined. This is illustrated in Table VI, which gives the transmittance of five sets of test solutions.

INTERFERING SUBSTANCES

Phosphates. The presence of phosphates gives high results in terms of ethylenediaminetetraacetic acid, as these compounds sequester some of the nickel, which on subsequent liberation would be interpreted colorimetrically as corresponding to Sequestrene NA3. Interference by small amounts of orthophosphates can be avoided by precipitation as calcium phosphate according to the procedure below.

REAGENTS. Calcium acetate, reagent grade, 44 grams per liter of distilled water. Other reagents same as given above.

PROCEDURE. To 98.5 ml. of clear sample adjusted to pH 6.5 add 15.0 ml. of nickel solution. Allow to stand for 10 minutes, add 1.5 ml. of calcium acetate solution, and then add 5 ml. of C.P. ammonia (28%). After 5 minutes filter from the precipitated calcium phosphate. To 60 ml. (one half of original) of filtrate add 7.5 ml. of dimethylglyoxime solution and after 5 minutes filter through No. 40 Whatman filter paper. To 50 ml. of filtrate add 2.5 ml. of concentrated hydrochloric acid (pH should be 1); after 5 minutes add 10 ml. of freshly prepared potassium dithiooxalate solution, and after 3 to 4 minutes introduce 1.2 to 1.4 grams of solid sodium acetate crystals with stirring to dissolve (pH 3.5 to 4). Make spectrophotometric measurements immediately at 508 mμ in 1-cm. cells, using a blank as reference.

DISCUSSION. In order to use the typical calibration curves (Figures 2 and 3), it is necessary to correct for the volume of added calcium acetate. As Figures 2 and 3 are based on a volume (sample-water) of 100 ml., the volume of added calcium acetate solution must be part of the 100 ml. In this particular case the actual sample (sample-water) volume would be 98.5 ml. (plus 1.5 ml. of calcium acetate solution, 100 ml.). This must be taken into consideration when making calculations.

A test solution containing 4 mg. of Sequestrene NA3 and 10 mg. of anhydrous disodium phosphate in 98.5 ml. of distilled water treated as above showed 62.5% transmittance. A test solution of 4 mg. of Sequestrene NA3 in 100 ml. of distilled water without disodium phosphate showed 61.5% transmittance.

Citrates. Citrate if present as ammonium citrate has a slight sequestering effect on the nickel and would tend to give slightly higher results. However, if the citrate is present as sodium citrate, there is no sequestering of nickel under the test conditions, with 20 mg. of sodium citrate in 100 ml. of test solution.

In the presence of up to 20 mg. of citric acid per 100 ml. of test solution, the citric acid is first neutralized to pH 6.5 with 0.5 *N* sodium hydroxide before addition of nickel solution. Also, as in the procedure for phosphates, the volume of 0.5 *N* sodium hydroxide added in this case must be allowed for in making up the 100 ml. of test solution and calculating the weight of the sample. A test solution containing 4 mg. of Sequestrene NA3, 10 mg. of sodium citrate, and 4 mg. of calcium as calcium acetate in 100 ml. of distilled water showed 62% transmittance in the test. A test solution containing 4 mg. of Sequestrene NA3 without calcium and sodium citrate showed 61% transmittance using a blank as reference.

Copper. Copper seriously interferes with the method, because it forms brownish complexes with the reagents employed. The complex partially precipitates. For this reason, and because the copper might displace some of the nickel in the test method, the setting up of a two-component color system (copper and nickel) would give very uncertain results. However, the copper can be removed and the test then carried out. 5,7-Dibromo-8-hydroxyquinoline (*2*) was found to be ideally suited as a precipitant for copper in the test procedure. It precipitates copper in acid solution and its spectral absorption under the test conditions is nil at 508 mμ.

REAGENTS. 5,7-Dibromo-8-hydroxyquinoline (Eastman), 0.5 gram in 40 ml. of C.P. hydrochloric acid and 60 ml. of distilled water. Other reagents same as previously given.

PROCEDURE. To 88.3 ml. of clear, neutral, or faintly acid (hydrochloric acid) sample add 11.2 ml. of 5,7-dibromo-8-hydroxyquinoline solution. The precipitate forms slowly. Allow to stand 15 minutes before filtering. If precipitation of copper does not start within 5 minutes, add a small amount (0.2 gram) of sodium acetate to lower the hydrochloric acid content slightly. Filter, and to 80 ml. of the filtrate add C.P. ammonia (28%) to neutralize. About 3 to 3.5 ml. of ammonia will be required to obtain a pH of 6.5. Add 12 ml. of nickel solution and allow to stand 10 minutes. Add C.P. ammonia (28%) to give a total of 5 to 6 ml. of ammonia (about 2.5 ml. in addition to the approximately 3.5 ml. of ammonia required for neutralization) and bring the pH to 11. Add 12 ml. of dimethylglyoxime solution with stirring. After 5 minutes filter through No. 40 Whatman filter paper and to 50 ml. of filtrate add 2.5 ml. of C.P. concentrated hydrochloric acid (pH now 1). After 5 minutes add 10 ml. of potassium dithio-oxalate solution with stirring. Allow the color to develop for 2 to 3 minutes and then introduce 1.5 to 2 grams of solid sodium acetate to give a pH of 3.5 to 4 and determine transmittance at 508 mμ using 1-cm. cells.

DISCUSSION. At the stage where the test solution is made alkaline with ammonia, the remaining excess of 5,7-dibromo-8-hydroxyquinoline is largely precipitated. This does not interfere with the precipitation of the nickel by dimethylglyoxime, both being filtered off together. Any 5,7-dibromo-8-hydroxyquinoline remaining in solution after addition of the ammonia will not influence the measurements because it does not absorb at 508 mμ.

In the analytical procedure given, the volumes of reagents, sample, etc., have been so adjusted that the results of transmittance measurements may be compared directly with the typical calibration curves in Figures 2 and 3. The amount of Sequestrene NA3 found will pertain to 88.3 ml. of sample.

A test solution containing 4 mg. of Sequestrene NA3, 10 mg. of cupric sulfate crystals, and 2 mg. of calcium in 88.3 ml. of distilled water and treated as above showed 62% transmittance, using as a reference a blank made up as above containing 10 mg. of cupric sulfate but without Sequestrene NA3 and run through the procedure in the same way as the test solution. The 62% transmittance is in agreement with 61% transmittance for a 4-mg. Sequestrene NA3 test solution, obtained in the procedure in the absence of copper.

COLOR STANDARDS FOR USE WITH NESSLER CYLINDERS

Suitable color standards may be employed in lieu of spectrophotometric equipment. The colors obtained in the test solutions show some fading after several hours and therefore are not suitable as permanent or semipermanent standards.

Color standards having reasonable stability were prepared with certain dyestuffs to match the colors of the following test solutions. Solutions containing 8, 4, 1, and 0.0 mg. of Sequestrene NA3 were diluted to 100 ml. and treated in accordance with the analytical procedure. In Table VII are given the compositions of color standards which match the test solutions when equal volumes are compared in matched Nessler cylinders.

Table VII. Composition of Color Standards

Dyestuff Solutions.
A. 0.050 gram of Solantine Pink 4BL (National Aniline Division, Allied Chemical and Dye Corp.) (C.I. 353) per liter of distilled water.
B. 0.0126 gram of Calco D.C. Brown No. 1 per liter of distilled water

Original Test Solution, Mg.	Composition of Color Standard, Ml.		
	A	B	Distilled water
8	45	2	53
4	18	2	80
1	6.5	3.5	90
0.0	0.3	4	96

The standards given in Table VII are illustrative. By following the same procedure, any number of intermediate standards may be prepared to cover any desired range. The standards are fairly close matches to the test colors. It is, however, very important that each user should check the standards against knowns. Corrections for any variation in dyestuffs or in individual technique, color discrimination, etc., may then be made by changes in the proportions of solutions A and B and water. The standards should be kept in closed glass bottles or Nessler cylinders in the dark when not in use. After 2 months the standards are somewhat paler and slightly yellower; therefore their color should be checked after 1 month and a new set prepared if necessary. The color standards must not be used in connection with the spectrophotometer, as the coloring substances in the test solutions and in the color standards are not the same, and the spectral transmittance will not be the same.

APPLICATIONS

The method is suitable for determining total ethylenediaminetetraacetic acid salts in industrial waters and solutions containing ethylenediaminetetraacetic acid with due regard given to pH and the possible presence of interfering substances or other nickel-complexing compounds.

In Alkali Metal Soaps. The following experiments indicate that the method is of value in determining Sequestrene NA3 in soaps.

To 99.5 ml. of aqueous solution containing 4 mg. of Sequestrene NA3 and 0.050 gram of Lux soap flakes was added 0.5 ml. of 4.4% aqueous C.P. calcium acetate solution. The soap was precipitated as the calcium salt and was filtered off after 5 minutes. To 50 ml. of filtrate were added 7.5 ml. of nickel solution. After standing 10 minutes 2.5 ml. of C.P. ammonia (28%) and 7.5 ml. dimethylglyoxime solution were added, and the samples were filtered after standing 5 minutes. To 50 ml. of filtrate were added hydrochloric acid, potassium dithio-oxalate, and sodium acetate as described in the analytical procedure.

Transmittance measurements were made at 508 mμ in 1-cm. cells, using as a reference a soap solution made up without Sequestrene NA3, but carried through the procedure as above with the blank set at 100% transmittance.

The transmittance of the test solution which originally contained soap was 64%, while the transmittance of a similar solution which did not contain soap was 61.5%. The method can be adapted for soap plant control. For such applications preferably soap solutions containing known amounts of Sequestrene NA3 should be used in setting up calibration curves.

In Urine. In connection with certain types of biological research employing ethylenediaminetetraacetic acid, a method for the determination of ethylenediaminetetraacetic acid in urine is of some importance. The following experiment in duplicate was made with this in mind.

An 8-mg. Sequestrene NA3 test solution was prepared, using as the sample 50 ml. of urine diluted with 50 ml. of distilled water. To the sample were added 15 ml. of nickel solution; after 10 minutes 5 ml. of c.p. ammonia (28%) and 15.5 ml. of dimethylglyoxime solution were added. After 2 minutes the sample was stirred with 3 grams of Nuchar C115 (activated carbon from Industrial Chemical Sales, New York, N. Y.) as a decolorizing agent. The solution was filtered after 5 minutes. The filtrate had a very pale yellow color. A further addition of 4 grams of Nuchar C115 was made and the sample again filtered. The filtrate was now practically colorless. To 50 ml. of filtrate were added 2.5 ml. of c.p. concentrated hydrochloric acid, 10 ml. of potassium dithio-oxalate solution, and 1.2 grams of sodium acetate, as described in the analytical procedure.

Spectrophotometric measurements at 508 mμ, in 1-cm. cells showed transmittances of 39 and 40%, which is in fairly close agreement with transmittances of 37 and 38% for test solutions containing 8 mg. of Sequestrene NA3 in 100 ml. of distilled water. A procedure based on calibrations employing urine dilutions containing known amounts of Sequestrene NA3 could be used instead of decolorizing with Nuchar.

ACKNOWLEDGMENT

For many helpful suggestions the writer is indebted to H. W. Zussman, who instigated this work. Thanks are due to A. A. Dolnick for helpful criticism.

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Received April 12, 1951. Published with the permission of Alrose Chemical Co., Providence, R. I. Sequestrene is the registered trade-mark of Alrose Chemical Co. for ethylenediaminetetraacetic acid and its derivatives.

Factors Affecting the Determination of Protein-Bound Iodine in Serum

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In order to ensure success with Chaney's method for the determination of protein-bound iodine, a study was made of the factors involved. The chemistry of the reactions was studied, and the effect of variations in method and the kinetics of the ceric sulfate–arsenious acid reaction was determined. The resulting information makes possible successful use of the method, even by technicians with limited training in chemistry.

FOUR basically different methods for the determination of protein-bound iodine have been reported (*2*, *6*, *7*, *10*). The method of Chaney (*2*) has been successfully employed in this laboratory with some slight modifications, but in some cases it was apparently unworkable. Further investigation showed in these cases an inadequate knowledge of the reactions involved or the factors influencing them. Accordingly, a study of the factors affecting Chaney's method was undertaken, which ranged from the determination of impurities in the various reagents to the determination of constants of the ceric ammonium sulfate–arsenious acid reaction. The results are presented for the consideration of chemists, but should also lead to a greater degree of accuracy in the work performed by technicians of limited chemical training and ability. The data are applicable in varying degree to methods that employ precipitation of the bound iodine, acidic wet washing, distillation into a base, or the catalytic effect of iodide on ceric ion reduction by arsenious acid.

REAGENTS

Redistilled water is distilled from an all-glass still containing a few pellets of sodium hydroxide. Unless otherwise indicated, all references to water imply redistilled water.

Sulfuric acid, 0.67 *N*.

Sodium tungstate, 10%.

Sulfuric acid, 70% by weight.

Chromic acid, 60% by weight.

Sodium hydroxide, 1%.

Phosphorous acid, 30% by weight. The prepared reagent supplied by J. T. Baker Chemical Co. has been found consistently satisfactory.

Superoxol, 1 to 10 by volume.

Arsenious acid, 0.064 *N* in 0.6 *N* sulfuric acid is prepared by dissolving 3.18 grams of reagent grade arsenious acid in 100 ml. of 1.4% sodium hydroxide in a 1-liter volumetric flask. The solution is diluted to about 500 ml. with water and 17.8 ml. of concentrated sulfuric acid are added. The solution is then made up to volume with water.

Ceric ammonium sulfate, 0.012 *N* in 1.6 *N* sulfuric acid is prepared by dissolving 7.16 grams of reagent grade ceric ammonium sulfate in approximately 900 ml. of 1.6 *N* sulfuric acid in a 1-liter volumetric flask and diluting the solution to volume with the acid. Slight precipitation will occur over a period of time, but this is not important if the clear supernatant liquid is employed.

Standard iodide solutions. Standards containing 0.04, 0.08, and 0.12 microgram of iodide per ml. are stable for 2 to 4 months if kept in a cool dark place.

PROCEDURE

The following brief description indicates minor changes from the Chaney procedure in reagent strength or technique which the author has found advisable.

Three milliliters of serum are added to a large centrifuge tube containing 3 ml. of 10% sodium tungstate solution and 20 ml. of water, 3 ml. of 0.67 *N* sulfuric acid are then added, and the mixture is well stirred with a rod. The precipitate is separated and is twice washed with 20-ml. portions of water, employing centrifugation.

Twenty milliliters of 70% sulfuric acid are added to the precipi-

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tate. The well-stirred mixture is then poured into a digestion flask containing a few glass beads and 2 ml. of 60% chromic acid. The centrifuge tube is washed with 20 ml. more of 70% sulfuric acid, which are added to the flask. The flask is placed on a hot heater. The mixture is brought to a boil and boiled for 3 minutes, after which the flask is removed from the hot plate and allowed to cool for 5 to 10 minutes. Then 20 ml. of water are added to the flask, which is replaced on the heater and allowed to boil until it is well filled with thin foglike fumes. The flask is removed from the hot plate and allowed to cool for 5 to 10 minutes, after which 10 ml. of water are added.

The distillation apparatus is now washed with copious amounts of water, care being taken that no air bubbles remain in the return tube after washing. The stopcock is closed and 1 ml. of 1% sodium hydroxide is introduced through the top opening; the return tube is avoided, so that the sodium hydroxide collects in and effectively blocks the trap. The flask is attached to the distillation apparatus and the side-necked dropping funnel with its stopcock closed is inserted into the flask. The entire apparatus is now lowered onto a hot heater, after which 10 ml. of 30% phosphorous acid are introduced into the dropping funnel.

Violent bumping may occur during this initial phase of heating, but tapping of the heater will help prevent it. After the mixture reaches a steady boil and before any distillate collects in the trap, the 10 ml. of 30% phosphorous acid are quickly blown into the flask, immediately followed by 1 ml. of 1 to 10 Superoxol introduced in the same manner. Distillation is allowed to proceed for 10 minutes. At the end of this period the dropping funnel is removed, the entire apparatus lifted off the heater, and the flask disconnected. The distillate is collected in a calibrated 15-ml. centrifuge tube containing 0.25 ml. of the arsenious acid reagent and allowed to cool to room temperature. The volume is noted. The distillation apparatus is washed and is ready for the next distillation.

One milliliter of 0.64 N arsenious acid is added to each colorimeter tube; 4 ml. of water are added to the first tube which serves as a blank for the ceric reaction, and 3 ml. of water plus 1 ml. of iodide standard are added to the next three tubes. The standards should contain, respectively, 0.04, 0.08, and 0.12 microgram of iodide. Four milliliters of distillate, in duplicates, are added to the remaining tubes. After thorough mixing, the tubes are ready for the addition of the 0.012 N ceric ammonium sulfate solution and may be kept in this state for several hours. When ready, 1 ml. of the ceric solution is added to each tube at exactly 30-second intervals and well mixed after each addition. The first tube is read in the photometer (420 mμ) exactly 20 minutes after the addition of the ceric ammonium sulfate and the subsequent tubes are read in order at 30-second intervals.

CALCULATIONS

The optical densities of the standards are plotted against their concentrations on ordinary graph paper. The optical densities of the unknowns can then be translated into concentrations. Then,

$$\frac{\text{Concentration of unknown} \times \text{volume of distillate} \times 100}{\text{amount of distillate used} \times \text{ml. of serum used}} = \text{iodine in micrograms per 100 ml. of serum}$$

From this value must be subtracted the amount determined for the reagent blank, obtained by running a blank through each step beginning with the digestion. The final value represents the amount of protein-bound iodine in micrograms per cent.

TESTING OF REAGENTS

A convenient method of determining the purity of reagents takes advantage of the fact that the proportions of the reagents may be varied under proper conditions without influencing the accuracy of the over-all procedure.

The purity of the reagents in the ceric sulfate–arsenious acid reaction is of prime importance.

One and 0.5 ml. of arsenious acid reagent are added to colorimeter tubes containing, respectively, 4.0 and 4.5 ml. of water; 1 ml. of ceric ammonium sulfate solution is added to each and mixed well. An initial reading is immediately made in the photometer (420 mμ), followed by readings at 10-minute intervals for 1 hour. There should be no appreciable decolorization in either tube. If decolorization occurs, interpretation is as follows: Equal decolorization in each tube indicates contaminated ceric ammonium sulfate, less decolorization in the second tube indicates contaminated arsenious acid, and about 10% greater decolorization in the second tube indicates contaminated water. Experience indicates that these reagents are not likely to be contaminated.

The precipitating reagents are tested by precipitating and washing (in the manner outlined in the procedure) 180 mg. of crystalline bovine albumin contained in 3 ml. of 0.9% sodium chloride and then carrying on the digestion, distillation, etc. The iodine value is compared with that obtained from 180 mg. of crystalline bovine albumin added directly to a digestion mixture. If contamination is demonstrated, addition of 3 ml. of each reagent to individual digestion flasks and subsequent determination of iodine will indicate the contaminated reagent. The testing must involve precipitation of proteins, as the washing of the precipitate effectively removes inorganic iodides not present in too large amount (Table I), whereas direct testing of the reagents may reveal iodide present in mild amount in the tungstate or in the sulfuric acid, giving cause for needless worry.

Table I. Effect of Different Precipitants on Recovery of Protein-Bound Iodine

(Deviations are standard deviations based on ten or more determinations in each category.)

Precipitant Employed	Mean Value Pooled Serum, γ % of Iodide Ion	Mean Value after Adding and Washing 3γ of Iodide	Iodide Retained in Precipitate, %
Acetic acid	6.0 ± 0.2	7.4 ± 0.3	1.4
Zinc	5.8 ± 0.1	7.5 ± 0.4	1.7
Trichloroacetic acid	6.1 ± 0.3	8.1 ± 0.5	2.0
Tungstic acid	6.0 ± 0.1	7.6 ± 0.4	1.6

Sulfuric acid (70%) is easily tested by adding 20, 30, and 40 ml. of the acid to digestion flasks containing 2 ml. of 60% chromic acid and then continuing the procedure to final determination.

In the author's experience the chromic acid accounts for 80 to 95% of the blank and should be chosen with care. Technical grade flakes frequently show less contamination than reagent grades. The degree of contamination is ascertained by using 1 and 2 ml. of 60% chromic acid in the digestion blanks. Acceptable chromic acid contains not more than 3 micrograms % of iodine. The contamination is reduced to less than 0.5 microgram % by boiling 400 ml. of the 60% chromic acid to the spattering point in a 3-liter round-bottomed boiling flask containing glass beads. By successive addition of 300 ml. of water the boiling is repeated three times, and after the final boiling the acid is diluted to the original volume with water.

Purity of the 1% sodium hydroxide is determined through the ceric sulfate–arsenious acid reaction. To colorimeter tubes containing 3.9 and 3.7 ml. of water, 0.1 and 0.3 ml. of the 1% sodium hydroxide are added, and 1 ml. of arsenious acid solution followed by 1 ml. of ceric ammonium sulfate solution is added to each tube. Initial readings are made, followed by readings at 10-minute intervals for 1 hour.

Contamination of the Superoxol is determined by using 1 ml. of a 1 to 20 dilution and 1 ml. of 1 to 10 dilution during distillation of reagent blanks. Experience indicates that this reagent is iodine-free.

Purity of the 30% phosphorous acid is easily ascertained by using 8, 10, and 12 ml. during distillation of reagent blanks.

FACTORS INFLUENCING THE DETERMINATION

Precipitants. Various means of precipitating the serum samples were tried. The acetic acid method detailed by Salter and McKay (*8*), the zinc precipitations described by Taurog and Chaikoff (*11*) and by Barker (*1*), trichloroacetic acid precipitation, and the method described in this report gave similar results (Table I). However, the use of trichloroacetic acid requires great care during the digestion to ensure removal of chlorides, which contribute to grossly erroneous results. The tungstic acid

Table II. Effect of Added Chloride on Iodine Determination

(Deviations are standard deviations based on six or more determinations in each category.)

NaCl Added to Digestion Flask, Mg.	Mean Values of Iodide Ion, γ %		
	3-minute digestion	5-minute digestion	Complete digestion
3	12.8 ± 0.8	7.1 ± 0.7	5.4 ± 0.2
15	13.0 ± 2.1	10.4 ± 1.1	5.7 ± 0.1
30	14.2 ± 1.6	12.2 ± 1.3	5.3 ± 0.3

Table III. Expulsion of Chlorides from Digestion Mixtures Containing No Iodine

(Deviations are standard deviations based on ten or more determinations in each category.)

Duration of Boiling, Min.	Enhancing Effect of Chloride on 5.0 Micrograms % of Iodide Ion		
	1.0 mg. NaCl	5.0 mg. NaCl	20.0 mg. NaCl
0	6.4 ± 0.3	9.6 ± 1.2	16.4 ± 1.6
2	5.4 ± 0.4	6.3 ± 0.5	12.3 ± 1.2
3	5.2 ± 0.2	6.1 ± 0.1	8.4 ± 0.4
Faint SO_3 fumes	5.0 ± 0.2	5.1 ± 0.2	5.0 + 0.1

precipitation was chosen because of its common use for other tests. It was found that two to three washings removed approximately 98% of 3 micrograms of iodide added to 3 ml. of serum before precipitation (Table I).

Digestion. The digestion procedure is a frequent source of error for the analyst unfamiliar with it. The procedure entails digestion of the proteins with concomitant liberation of the bound iodine, which is then oxidized to iodate. The concurrent expulsion of chlorides must be complete or the iodine effect is enhanced. This enhancing effect was first reported by Sandell and Kolthoff (*9*) and examined in detail by Barker (*1*), who employed it in the ceric reaction. The effect has been studied in this laboratory to determine fluctuations in apparent values caused by adding chlorides to the precipitated protein mass (Table II). The expulsion of chlorides from digestion mixtures containing no iodine was then studied (Table III). To the distillates were added equal amounts of iodide and the apparent values were noted against a standard containing no chloride. As a result, the digestion has of necessity two definite boiling periods. The first boiling serves to digest the greater percentage of the proteins and allows the iodine to be converted to iodate. Boiling is stopped as soon as the faintest fumes appear. Strenuous boiling is avoided, to prevent loss of iodine before it is converted to nonvolatile iodate. In the second period, however, strenuous boiling is encouraged and continued until the flask is well filled with fumes which are not overly dense. This serves effectively to expel chlorides while retaining iodates.

Table IV. Loss of Protein-Bound Iodine with Prolonged Boiling of Digestion Mixture

(Deviations are standard deviations based on fifteen or more determinations in each category.)

Duration of Boiling Past Faint SO_3 Fumes, Min.	Iodide Ion, γ %
1	5.0 ± 0.3
3	4.1 ± 0.5
5	3.6 ± 0.3
10	1.4 ± 0.2

The importance of stopping the boiling at this point cannot be overemphasized. It is, in the author's opinion, the most critical point of the entire determination. If the boiling is allowed to continue until very dense fumes fill the flask, loss of iodine will occur (Table IV). The loss is probably occasioned by a reduction of the iodate, for at this point a partial reduction of the chromic acid blank is evidenced by a slight greenish discoloration. It is unfortunate that no exact time can be assigned to the boiling periods, and each laboratory must determine for itself the time to be employed. Of prime importance for good duplicable results is a constant nonfluctuating source of heat. In this laboratory, Cenco Hotcone heaters were found far superior to gas or electric plate heaters.

Distillation. Barker (*1*) and Taurog and Chaikoff (*11*) have discussed the distillation procedure. The former reported a recovery of 0 to 10% following Chaney's method, while the latter reported an average recovery of 87% following the same method. Barker then substituted sodium sulfite for sodium hydroxide in the trap and subsequently had recoveries averaging 90%. Experiments were conducted in this laboratory to seek an explanation for the discrepancy between the two papers.

Iodide (0.12 microgram) was added to 3-ml. aliquots of pooled sera which had a determined average value of 0.058 microgram per ml. The extent of recovery was then ascertained, employing varying concentrations of phosphorus acid with and without peroxide (Table V). The results ranged from a low (18 to 42%) recovery for the theoretical amount of phosphorus acid used alone, to a high (88 to 94%) recovery for an increased amount of phosphorus acid with hydrogen peroxide.

In each case the extent of recovery was roughly proportional to the time of distillation; this indicated that the iodate was not immediately reduced to hydriodic acid. The poor recoveries can be explained on the grounds that reduced iodate distilled as hypoiodite, iodine, and hydriodic acid. The first two react with the sodium hydroxide in the trap to produce sodium iodate along with sodium iodide and sodium hypoiodite. Furthermore, the iodide and hypoiodite react with each other (*4*), liberating more iodine, which in turn reacts with the sodium hydroxide to produce more iodate. Under such conditions a substantial amount of iodate is present in the distillate.

Table V. Recovery of Added Iodide during Distillation

(Effect of varying concentration of phosphorus acid, absence or presence of hydrogen peroxide, and varying duration of distillation. Added iodide varied from 0.03 to 0.30γ. Range of percentage recovery is total range observed.)

Volume of Distillate, Ml.	Duration of Distillation, Min.	Recovery of Iodide Added to Precipitated Serum, %			
		8 ml. 30% H_3PO_3	8 ml. 30% H_3PO_3, 1 ml. 1–10 H_2O_2	10 ml. 30% H_3PO_3	10 ml. 30% H_3PO_3, 1 ml. 1–10 H_2O_2
5–6	4	12–18	40–50	20–34	60–70
6–8	6	14–18	40–70	25–40	74–89
8–10	8	14–35	60–80	30–45	80–90
10–13	10	18–42	70–80	30–50	88–94

Experiments showed that iodate does not catalyze the ceric sulfate reaction as does iodide, strengthening the assumption that the distillate contained both iodide and iodate. The use of sodium sulfite in place of sodium hydroxide as proposed by Barker would eliminate this difficulty, but as the resultant sulfurous acid also reduced ceric sulfate, it had to be eliminated prior to the ceric sulfate reaction. Its removal was too cumbersome for routine use. The addition of arsenious acid to the sodium hydroxide resulted in a distillate which caused an immediate partial reduction of the ceric ammonium sulfate. The reduction proved to be independent of the amount of iodide present in the distillate and experiments along those lines were terminated. Thomas *et al.* (*12*) have published a modification employing arsenious acid and sodium hydroxide, which is apparently successful. In later experiments, conducted after publication of Thomas' proposal, the same partial decolorization was obtained. Therefore the author feels that the original decision to focus attention upon the complete reduction of iodate prior to distillation was the only satisfactory answer to the problem of obtaining high yields.

In practice, a ratio of about 3 grams of phosphorus acid to

2 grams of chromic acid assures adequate reduction of the iodate in the digestion flask. It appears that 100% recovery is impossible, as almost half of the reduced iodate is distilled in the first few minutes and a very small amount is distilled as iodine, resulting in the formation of iodate. As the use of peroxide increases the recovery, in this instance it must act as a reducing agent, reducing liberated iodine to hydriodic acid in the digestion flask.

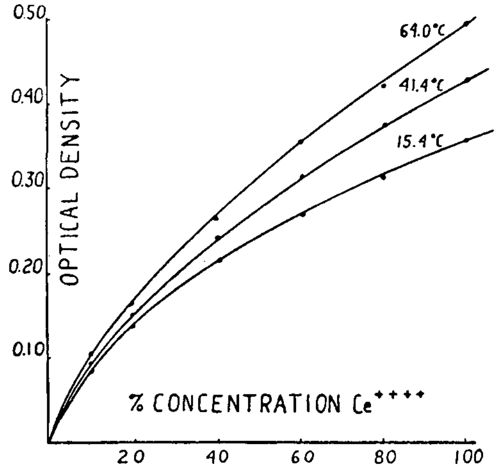

Figure 1. Relationship between Optical Density and Concentration of Ceric Ammonium Sulfate at Varying Temperatures

If it is postulated that the iodate forms complex acids with the chromic acid, it is possible to understand why the iodate is not quickly and completely reduced to hydriodic acid in the presence of a powerful reducing agent. It is equally evident that the iodate may then be distilled as hypoiodite, iodine, or hydriodic acid. Although this deduction was not made by Barker, data in his paper corroborate this point. The discrepancy between Barker's recovery of 0 to 10% when employing sodium hydroxide and Taurog's and Chaikoff's recovery of 87% can then be explained. In Barker's case the reduction of iodate was not complete and resulted in the distillation of hypoiodite which was converted by sodium hydroxide to iodate, whereas in Taurog's and Chaikoff's case the distillation product was hydriodic acid (with some iodine), resulting in the formation of iodide. Barker's reagents differ from Chaney's in that the former are upon a weight per volume basis and the latter's are on a weight per weight basis. Thus Barker's reagents are appreciably weaker than Chaney's.

A final factor influencing the recovery is the rate at which the digestion mixture is boiled during distillation. It would appear that a slow moderate rate would give best results, in so far as it permits complete reduction of the iodate. Such is not the case (Table VI).

Table VI. Effect of Varying Rate of Distillation on Recovery of Added Iodide

(Added iodide varied from 0.30 to 0.30 γ. Range of percentage recovery is total range observed)

Rate of Distillation		Recovery of Added Iodide Ion, %
Ml.	Min.	
12	6	78-92
12	10	88-94
12	20	65-85

Summarizing, phosphorus acid should be employed in excess and should be quickly added after brisk boiling has set in, the use of hydrogen peroxide should not be disregarded, and the distillation should be briskly carried on for an adequate time.

Catalytic Reaction. The reduction of ceric ammonium sulfate by arsenious acid is complex. Two salts of ceric ammonium sulfate exist, one yellow and the other orange yellow (*5*). The ratio of one to the other is not fixed, but is dependent upon the mode of preparation. In addition, it appears that in solution a highly colored intermediary reduced form exists (*5*). This reduced form, cerosoceric hydrosulfate, does not occur in a known definite percentage nor is it readily related to the amounts of ceric and cerous sulfate present, although some definite relationship must exist. This is substantiated by the fact that optical density-concentration curves for ceric ammonium sulfate at different temperatures (Figure 1) form a family of curves and, given several of these curves, it is possible to plot a curve for an arbitrary temperature within 5 to 10% of the experimental curve for that temperature. During catalysis the state of the reagents is in flux and it has been impossible in this laboratory to determine the exact composition of the state at a given time. The only statement that can be made at present is that the reduction proceeds in an orderly although complex fashion to finality when a colorless solution of cerous sulfate exists.

Table VII. Pseudo-First-Order Rate of Ceric Ammonium Sulfate–Arsenious Acid Reaction, and First-Order Effect of Iodide Concentration

(Temp. 19.0° C.)

	Concentration of Iodide					
	0.04 γ		0.08 γ		0.12 γ	
Times, Sec.	% ceric ion in solution	$K \times 10^{-3}$	% ceric ion in solution	$K \times 10^{-3}$	% ceric ion in solution	$K \times 10^{-3}$
300	85	0.58	73	1.05	61	1.64
600	72	0.55	55	1.00	39	1.57
900	64	0.50	42	0.97	24	1.59
1200	54	0.53	29	1.06	14	1.68
1500	47	0.50	22	1.01	8	1.66
1680	42	0.52	18	1.02	6	1.67
Av. *K*	$(0.53 \pm 0.016) \times 10^{-3}$		$(1.02 \pm 0.015) \times 10^{-3}$		$(1.64 \pm 0.034) \times 10^{-3}$	

In view of the foregoing, it is understandable that dilutions of ceric ammonium sulfate do not follow Beer's law (Figure 1). However, with such a curve, optical density can be translated into per cent of ceric ammonium sulfate present. With this information and the equation $K = \frac{2.303}{t} \log \frac{a}{a - x}$ where a = initial concentration, $a - x$ = concentration after time t, and K = velocity constant, it can be demonstrated that the arsenious acid–ceric sulfate reaction is pseudo-first order (Table VII), if the arsenious acid is present in excess. From Figure 1 it is apparent that there is no special reason why the reaction must be run at an elevated temperature if blanks and standards are included; therefore it is the practice in this laboratory to run the reaction at room temperature. It is important, however, that the standards and unknowns be at the same temperature, since the optical density of the solution is increased by an increase in temperature. This can be achieved by letting the tubes stand in racks under identical conditions for approximately 20 to 30 minutes prior to the addition of ceric ammonium sulfate. Direct sunlight will catalyze the reaction, even in the absence of iodide, and proper precautions must be taken to prevent this effect.

It has not been found necessary to equilibrate the colorimeter tubes as suggested by Salter and McKay (*8*), and minor fluctuations in ionic strength appear to have no effect. Because standards are used, it is not necessary to standardize the arsenious acid against the ceric ammonium sulfate. The reaction is most sensitive if the normality of the arsenious acid is approximately 5 times that of the ceric ammonium sulfate. Therefore the strength of the ceric ammonium sulfate solution may be changed to meet the requirements of other types of photometers if the ratio is maintained. Very poor and erratic results occur if the reagents are of equal normality.

The best curve for routine use is obtained by using 0.04, 0.08, and 0.12 microgram of iodide (Figure 2). The slope of the curve will depend upon the reaction time and temperature. The average room temperature in this laboratory is 21° C. and the reaction time employed is 20 minutes. The curve is made by drawing a straight line between the points. Maximum deviation from the true curve is about 0.002 microgram. The curve, as given, is in the most accurate portion of the photometric readings, and therefore extension is not warranted. Furthermore, points based on 0.16, 0.20, and 0.24 microgram of iodide are so close at 20 minutes that accuracy in this range is nil. On the other hand, readings taken say at 10 minutes, when accuracy still exists in the high range, give very little accuracy in the range 0.01 to 0.08 microgram. This difficulty cannot be overcome by running the reaction at a higher temperature. It is possible, of course, to take readings at both time intervals, but higher standards must then be included. It is the practice in this laboratory to dilute samples that give very high results and make a second determination.

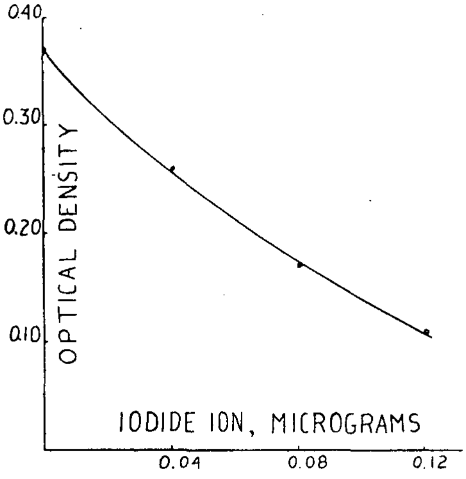

Figure 2. Standard Curve at 20 Minutes, 21° C.

Another source of error is in the construction of a nomogram as detailed by Salter and McKay (*8*). It is claimed that such plottings show the rate of reduction of the colored ion at any given concentration of iodide to be a linear function. Work done in this laboratory does not verify that statement. Instead, the function is a definite curve.

It is true that the reduction of ceric ammonium sulfate is pseudo-first order, but this holds only if the arsenious acid is in sufficient excess. The mathematical determination of the rate of reaction is dependent upon the actual concentration of ceric ion at any given instant. This concentration can be obtained for a particular temperature by the construction of a curve as in Figure 1, where known concentrations are plotted against their optical densities. Furthermore, the log of the rate of reaction *K* can be plotted against the reciprocal of the absolute temperature (Figure 3) and the resulting straight line establishes the first-order nature of the reaction. The effect of iodide concentration within the limits 0.01 to 0.15 microgram is first order, but deviates from first order outside these limitations.

It is important to remember that the concentration of the ceric ion does not obey Beer's law. From Figure 1 it can be seen that the curve of the plot is parabolic, and by taking the log of the concentration and plotting it against the log of the optical density a slightly curved line can be drawn (Figure 4). From this line a first approximation for the relationship of concentration to optical density can be derived. The equation, $y = 1.74 (x)^{0.67}$ (where y = optical density and x = concentration in %), is only approximately correct and does not hold in either the high or low values of x. On the other hand, the plotting of the reduction of the ceric ion (Figure 5) also presents a parabolic curve for the various concentrations of iodide. These latter curves are dependent upon the rate of the reduction, *K*, which is in turn dependent upon the concentration of iodide (Table VII) and temperature. If now, a composite graph showing the curve (*A*) for the relationship of ceric concentration against optical density and a standard curve (*B*) showing the reduction of ceric ammonium sulfate ion under catalytic effect be drawn (Figure 6), the one is a very rough reciprocal of the other. It is this canceling out effect which gives a semblance of linearity as drawn in Salter's nomogram. Because the concentration–optical density curve is comparatively constant (Figure 1) whereas the concentration-catalysis curve is sensitively subject to temperature, it can be shown that at room temperature the construction of

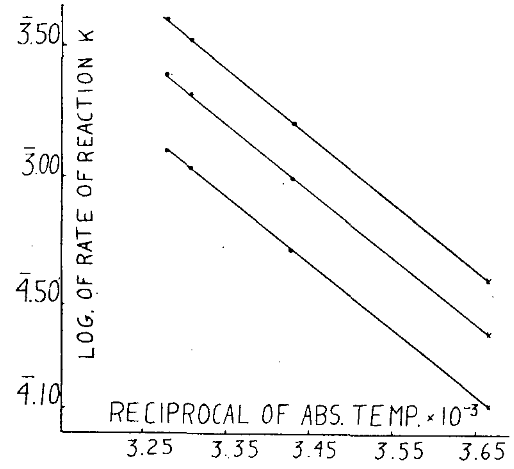

Figure 3. Log of Rate of Reaction *K* Plotted against Reciprocal of Absolute Temperature, Projected to Determine Rate of Reaction at 0° C.

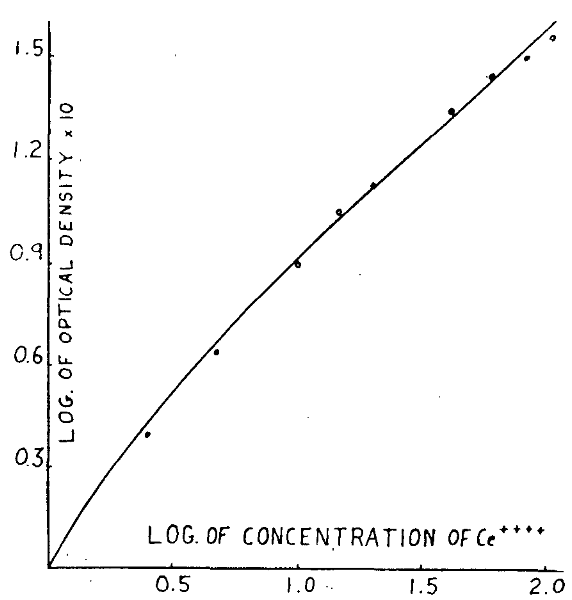

Figure 4. Log of Optical Density Plotted against Log of Concentration

Table VIII. Constants of Ceric Ammonium Sulfate–Arsenious Acid Reaction at Varying Temperatures

Iodide Ion, γ	Temp., ° C.	$K \times 10^{-3}$	ΔF, Cal. Mole^{-1}	$K_0 \times 10^{-3}$	ΔS, Cal. Deg.$^{-1}$ Mole^{-1}
0.04	16.8	0.46	21,440	0.172	−41.9
	19.4	0.53	21,510		
	30.0	0.93	21,970		
	37.2	1.33	22,270		
0.08	16.8	0.92	21,020	0.347	−40.5
	19.4	1.04	21,110		
	30.0	1.82	21,540		
	37.2	2.61	21,830		
0.12	16.8	1.40	20,720	0.525	−39.5
	19.4	1.61	20,810		
	30.0	2.83	21,250		
	37.2	4.03	21,510		

$Q = 9.27 \times 10^0$ cal. mole^{-1}
Temp. coefficient, 10° interval = 1.72

such a nomogram is demonstrably nonlinear. From a theoretical standpoint there is no reason why the rate of reaction which controls curve *B* should be inversely proportional to the concentration–optical density curve *A*. Close inspection of the nomogram presented by Salter, especially of the points formed by the 0.24, 0.21, 0.12, 0.08, and 0.06 microgram concentrations will bear out the preceding comments. In this nomogram the error is slight, as the curves are not pronounced, except in the high concentrations, and the readings were taken over an extended time. However, a gross error may easily result if the standard chart is made up from readings taken over a short period of time and then, during the actual determinations of unknowns, readings are taken at a much greater interval of time. In the low range, 0.01 to 0.04 microgram, the error may be as much as 0.01 microgram, while in the higher ranges the error may range as high as 0.06 microgram.

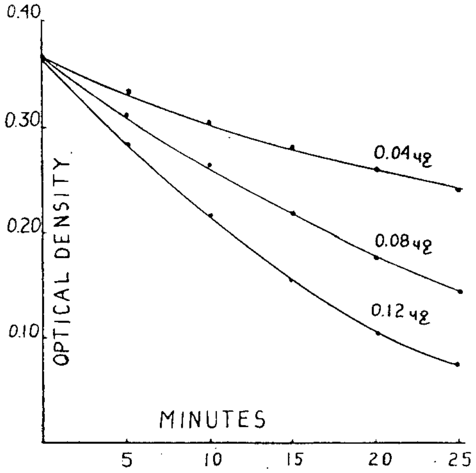

Figure 5. Reduction of Ceric Ion by Varying Iodide Concentrations at 19.1° C.

Constants of the reaction are given in Table VIII. K_0 (the velocity constant at 0° C.) was computed by extrapolating the lines formed by plotting the log of *K* of the iodide concentrations at varying temperatures against the reciprocal of their absolute temperatures (Figure 3). K_0 indicates the effect of the iodide concentration to be first order in the range given; therefore satisfactory accuracy should be obtained in running standards. *Q* is the activation energy for the reaction in calories per mole and is obtained by the equation

$$Q = R\,2.3\,\frac{(\log K_2 - \log K_1)}{(1/T_1 - 1/T_2)}$$

in which K_1 and K_2 are the rates at the absolute temperatures T_1 and T_2, and *R* is the gas constant in calories. ΔS, the entropy of activation, is obtained by the equation $K_0 = 5.7 \times 10^{12} \times e^{-Q/RT} \times e^{\Delta S/R}$ (5). The change in free energy, ΔF, is obtained from $\Delta F = \Delta H - T\Delta S$. The temperature coefficient for a 10° interval is derived from

$${\frac{K_1}{K_2}}^{\left(\frac{10}{T_1 - T_2}\right)}$$

The specific reaction rate for a given temperature can be derived from the empirical equation, $K = X[11 + 0.9(b - 16.8)] \times 10^{-3}$, where X = concentration of iodide and b = temperature in ° C. This equation is correct within 4% for temperatures between 17° and 55° C.

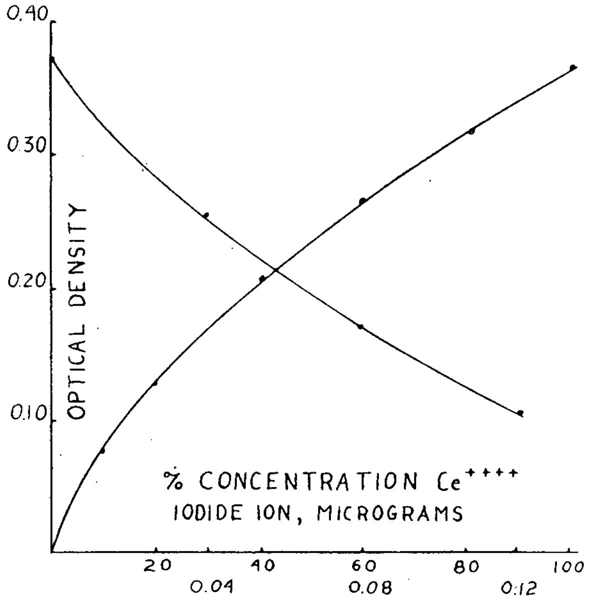

Figure 6. Comparison of Curve *A* for Optical Density of Per Cent Concentration of Ceric Ion and Curve *B* for Reduction of Ceric Ion Under Catalysis

Iodate in micro concentration does not catalyze the reaction, but if a few milligrams are employed, the reaction is completely catalyzed to a clear colorless solution, which then develops an orange color more intense than the original yellow. It is possible that the iodate liberates a few micrograms of iodine which are catalytic. It is obvious that a reoxidation has occurred, since the cerous solution is colorless, but the exact mechanism is puzzling. The intense coloration may be due to a reappearance of cerosoceric hydrosulfate in strong amounts. Both iodide and iodine catalyze the reduction of ceric ammonium sulfate to completion without a subsequent reappearance of color.

SUMMARY

An outline has been drawn up for systematically testing reagents to locate a source of contamination. The precipitant can be a matter of choice. The digestion procedure is subject to careful boiling to expel chlorides and retain iodine. The extent of recovery is dependent upon the amount of phosphorus acid employed, whether hydrogen peroxide is absent or present, and the rate and duration of distillation. The distillate will show low results if it contains iodate which does not catalyze the ceric sulfate–arsenious acid reaction. The kinetics of the ceric reduction with the concurrent effect of iodide ion are presented. The rate of reduction is found to be pseudo-first order and the effect

of iodide is first order. The catalytic reaction can be run at room temperature. The presence of sunlight will catalyze the reaction and is to be avoided.

ACKNOWLEDGMENT

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Quantitative Determination of Raffinose in Mother Beets and Raw Beet Juices

By Paper Chromatography

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Sugar beet breeders and others in the beet sugar industry have long sought a method for determination of raffinose, adaptable to volume operation and applicable to small samples, such as are available from single mother beets. The objects of the present investigation were to develop such a method, and to learn the raffinose content of individual roots, variations in raffinose content of different varieties, and change in raffinose content of roots during storage. The method described includes treatment of juice from the beet by mixed-bed ion exchangers, and a modification of deWhalley's method of paper chromatography for determination of raffinose in raw beet sugars. Individual roots of a single variety showed large variations in raffinose content, different varieties of beets showed significant differences, and all beets tested showed increase in raffinose content during storage. Use of the method enables the sugar beet breeder to test large numbers of beets for selection of those of low raffinose content. It also provides a tool, more dependable than the common hydrolytic procedures, for the study of factors that may determine the content of beet juices encountered in sugar manufacturing operations.

APPARENTLY all juice obtained from sugar beets contains some raffinose, the absolute quantity depending on environmental conditions under which the beets are grown and stored, and possibly on hereditary factors as well.

Because certain operating problems in beet sugar manufacture are increased as the raffinose content of the beet juice increases, the beet breeder has long sought a suitable method for raffinose determination in the hope that beet strains inherently low in raffinose content might be obtained through selection.

Chemical methods employing acid or enzyme hydrolysis are unsuitable from the beet breeder's viewpoint because they require large samples of material for analysis, are not readily adapted to volume operation, and do not yield dependable results on products containing a low ratio of raffinose to sucrose, as do normal sugar beets.

The method for determining raffinose in raw beet sugars by paper chromatography, recently published by deWhalley (*4*), provided the necessary lead, and a method that meets the beet breeder's requirements was developed. The method described, which is adaptable to volume operation, permits analysis of the small sample of rasped pulp, available from individual mother beets, for raffinose content and other components as well, with a satisfactory degree of accuracy.

The raffinose test consists of pressing a small quantity of juice from a portion of the pulp sample, preparing the juice for paper chromatography, and quantitatively by measuring the raffinose content of the prepared sample. The method is applicable to any juice or liquor, raw or defecated, encountered in the beet sugar manufacturing process.

PREPARATION OF SAMPLE

The beet roots from which breeding selections are to be made are carefully stored in a cellar between time of harvest and time of making selections.

Tests for various components under consideration are made on a sample of rasped pulp. A wide-angle rasp, which cuts a 36° sector from the root along the axis from tip to crown, is used to provide a sample of sufficient size from roots of minimum size. The minimum size of root normally encountered weighs about 700 grams, from which somewhat more than 60 grams of pulp may be recovered with care. After 13 grams of the pulp have been taken for determination of sugar and other components, the residual pulp is employed for the raffinose determination. Simultaneous determination of raffinose and other components will generally not be feasible, and therefore the residual pulp is placed in a small plastic bag, labeled, quickly frozen, and stored at a temperature below 0° F. until time for the raffinose determination. From results obtained to date, it appears that frozen pulp may be stored indefinitely without change.

Preparation of the sample for paper chromatography requires: pressing the juice from the pulp sample, deionizing the press juice sample; and adjusting the deionized sample to standard concentration.

A small hydraulic press, such as the Carver laboratory press, is suitable for rapid preparation of the desired volume of press juice. From 40 grams of pulp, wrapped in 16-ounce duck, more than 20 ml. of press juice may be obtained.

Partridge (*5*) noted a harmful effect from the presence of inorganic matter in paper chromatography of sugars and suggested use of ion exchangers for their removal. Albon and Gross (*1*) noted that the presence of more than 1.5% ash in raw sugars caused interference with the raffinose test, and also suggested use of ion exchangers.

The amount of ash carried by beet juice is well above the critical point, and therefore deionization is required.

Deionization is effected by means of a mixed bed consisting of 2 volumes of anion exchanger, such as IRA-400, and 1 volume of cation exchanger, such as IR-120. Anion exchangers of the type of IR-4B and IR-45 gave unsatisfactory results. The ion exchanger bed absorbs a small amount of sugar and furthermore absorbs sucrose and raffinose in different ratios. Obviously, the sucrose-raffinose ratio in the effluent must be the same as that in the original juice.

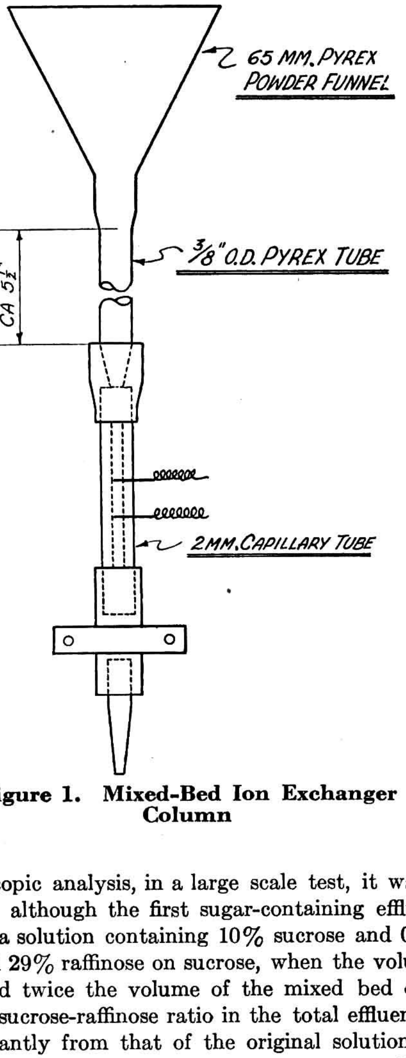

Figure 1. Mixed-Bed Ion Exchanger Column

By polariscopic analysis, in a large scale test, it was demonstrated that, although the first sugar-containing effluent from treatment of a solution containing 10% sucrose and 0.75% raffinose showed 29% raffinose on sucrose, when the volume of effluent equaled twice the volume of the mixed bed of ion exchanger, the sucrose-raffinose ratio in the total effluent did not differ significantly from that of the original solution.

Chromatographic tests have shown the proper raffinose content of the various samples of effluent from 5-ml. beds of ion exchanger when solutions containing 15% sucrose and 0.3, 0.5, and 0.7% raffinose on sucrose were treated and the effluents from each column were collected in three 10-ml. increments.

On occasion beet juices are encountered which contain a relatively small amount of ionic matter, and therefore permit the recovery of large volumes of deionized effluent. Tests were made on such juices to demonstrate the constancy of sucrose-raffinose ratios in the effluents. Effluents were caught in increments, each of a volume equal to twice the volume of the ion exchanger bed. The sucrose-raffinose ratio was found to be constant in all increments.

Finally, pure raffinose has been added to beet press juice and the deionization treatment given to both the original and the fortified juices. The chromatogram showed the expected increase in raffinose content of the fortified sample.

Absorbed sugars are displaced by absorption of ionic matter, of which beet juice generally contains a large quantity. The end point of the ion exchanger treatment may be taken as the point where ionic matter begins to break through the column in significant quantity, or the point where, for safety, the volume of effluent equals thrice the volume of the ion exchanger bed if ionic matter has not broken through in significant quantity at this point.

The mixed ion exchanger is placed in a column made from $^3/_8$-inch glass tubing, about 5.5 inches long, having a 2.5-inch funnel fused at the top, and a constriction at the bottom in which a loosely fitting cotton plug is placed. Below this is attached a crude conductivity cell consisting of a 2-mm. glass tube with two fused-in platinum wires 1 cm. apart. About 5 ml. of mixed ion exchanger are washed into the column; formation of air pockets is guarded against while filling. The water level is held at the surface of the ion exchanger bed until juice treatment starts. Figure 1 shows the deionizing column. Press juice is poured into the funnel and the flow rate is adjusted to about 1 ml. per minute. As soon as the water is displaced from the column (about 2.5 to 3 ml.), collection of the sample begins. At this point the resistance in the cell is above 100,000 ohms. Collection of the sample continues until 15 ml. are obtained or the resistance drops to 7000 to 8000 ohms. The end point may depend on the characteristics of the conductivity cell employed. One worker, operating a battery of five such columns, all connected to a suitable selector switch, encounters little difficulty after a short training period.

The deionized juice from normal beets, which is generally a dark, turbid liquid, is satisfactory for spotting on the paper, after adjustment of concentration to a standard value. A few drops of the effluent are tested for concentration in a refractometer, and a measured volume of the effluent is carefully diluted to standard concentration with water—generally 10 or 5% dry substance, depending on the raffinose content of the samples.

As results are reported as per cent raffinose on sugar, adjustment of concentration on a refractometer dry-substance basis involves some error, but not sufficiently great to be of significance in selection work. Purity determinations on a number of deionized press juice samples have given results of 95% or higher.

DETERMINATION OF RAFFINOSE BY PAPER CHROMATOGRAPHY

The procedure employed on beet juice follows generally that described by deWhalley (*4*) and by Albon and Gross (*1*) for raw beet sugars. It is necessary to select standards of the proper range for the beets under investigation. When working with freshly harvested beets, standards carrying 10% sucrose and from 0.2 to 1.0% raffinose on sugar in steps of 0.2% have been found satisfactory.

Twenty microliters of a 10% sugar solution, containing 1.0% raffinose on sucrose, carry 20 micrograms of raffinose—this is about the maximum quantity of raffinose per spot found by deWhalley (*4*) suitable for quantitative measurement. This quantity of sample applied in a single drop produces too large a spot for best results. Therefore the sample is applied to the paper in three approximately equal increments, and each increment is permitted to dry before application of another. A micropipet control, such as No. 293, Size A, marketed by the Micro Chemical Specialties Co., Berkeley, Calif., provides satisfactory control of delivery of the sample. The micropipets used in this work were prepared in the laboratory and all delivered 17.0 ± 0.25 microliters.

Little study of filter papers was made, and nothing superior to Whatman No. 1 was found.

The 22.5 × 18.25 inch sheets are cut to form two 22.5 × 9.125 inch sheets. The papers are spotted along a line 8 cm. from one end, at 3-cm. intervals; 5 spots of the standard raffinose solutions and 12 spots of juice samples are placed on each sheet. As a tendency often exists for the sample to climb the outside of the pipet tip, the paper is lifted to come in contact with the pipet tip before the micro-pipet control screw is turned to cause delivery of the sample. Mild heating, provided by a 60-watt silver bowl light globe, placed under the point of spotting, is used to hasten drying. The spotting bench carries three micropipets and heaters, all operated by one worker.

Chromatograms are run by the downflow procedure, using a wooden cabinet, heavily coated with paraffin, and stainless steel troughs. The paraffin coating is not sufficiently resistant to the vapors of the solvent employed, and requires care to maintain in proper condition. Stainless steel, or glass as described by deWhalley (*4*), is superior but was not available. For superior results, the cabinet needs to be vapor-tight.

Figure 2 shows the cabinet, and the simple stainless steel frame used to support the troughs. The troughs are made by cutting stainless steel pipe, 2 inches in outside diameter, along its axis, and welding on rectangular ends which serve as supports. Notches are cut just above the edges of the trough, and glass rods are held in the notches. This device prevents accidental siphoning of solvent from the trough to the filter paper sheet.

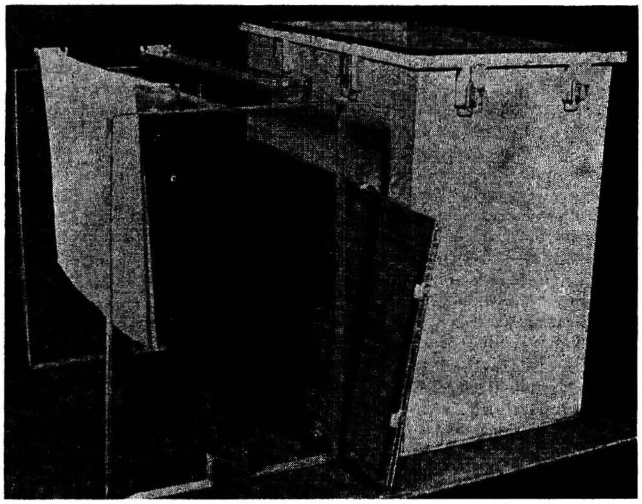

Figure 2. Chromatograph Cabinet, Trough Support, and Trough Assembly

The solvent used is a modification of that described by deWhalley (*4*) and is prepared by mixing 50 volumes of *n*-butyl alcohol, 30 volumes of pyridine, 30 volumes of water, and 4.5 volumes of benzene. This mixture forms a single phase which will not break into separate phases if the laboratory cools unduly overnight.

Spotted sheets of filter paper are placed in the troughs, and the chromatograms are started without pretreatment of the papers in saturated vapors. A large pan of used solvent is placed in the bottom of the cabinet.

Chromatograms are permitted to develop overnight and are then removed from the cabinet, dried in air, and finally in an oven at 90° C. for 1 hour.

Various color indicators have been tried, but none found equal to the 1% solution of 1-naphthol in ethyl alcohol plus 1 volume of phosphoric acid to 10 volumes of 1-naphthol solution, recommended by Albon and Gross (*1*).

Uniform spraying of the sheet is highly important and both sides are sprayed. After spraying, the sheet is permitted to dry in air for at least 30 minutes before heating. This drying treatment increases the sensitivity of the test and decreases relative background intensity. The sheet is then placed in a large oven at 90° C. and heated for 5 minutes for color development. Uniformity of oven temperature in the area where the sheet is placed is also highly important.

Immediately after removal from the oven, the sheet is cut into strips and unknowns are compared with the standards for measurement of raffinose content, using transmitted light. A view box covered with a milk glass plate uniformly illuminated from beneath serves well.

Figure 3 is a photograph of a finished chromatogram. Samples 1, 2, 8, and 9 are beet juices; No. 8 was held until decided deterioration had developed. Samples 3 to 7 are standards containing 0.2 to 1.0% raffinose on sucrose.

ACCURACY OF RESULTS

Probably the best basis for estimation of accuracy of results is comparison of results of replicate tests. If proper attention to details of spotting, spraying of paper, and heating to bring out colors is observed, replicates generally produce spots of the same intensities, and the standards invariably show the expected gradation in colors. The deionized beet juice carries more or less colloidal matter, which at times appears to cause some interference with the running of the sugars, with accompanying changes in the shape and size of the raffinose spot.

An idea of the accuracy of the method may be obtained from Table I, which shows observed differences in duplicate tests made on deionized juices from 204 individual beets. The mean of all tests was 1.33% raffinose on sucrose.

These results are satisfactory for purposes of selection. The beets being tested were abnormally high in raffinose content, and a given variation in intensity of spot color, between duplicates, resulted in twice the normal variation in raffinose found as all tests were run at a concentration of 50% of standard. In other words, when working with normal beets, using solutions at 10% dry substance, a maximum variation of 0.2% raffinose on sugar is expected in duplicate tests, and this variation but rarely.

Occasionally interference with the raffinose test arises from an extraneous sugar sometimes observed adjacent to the raffinose spot. While all normal beets show only sucrose, raffinose, and levulose, when 1-naphthol is used to develop the chromatogram, after too long storage of the beet roots or juice samples obtained therefrom, extraneous ketose-containing sugars may appear on the chromatogram. If any of these extraneous sugars appear, one is invariably observed which has an R_f value slightly greater than that of raffinose, and because the spot often borders that of raffinose it may interfere with the estimation of raffinose intensity. Conceivably this sugar is one, described by Blanchard and Albon (*3*), which is found in sugar liquors incompletely hydrolyzed by invertase. Bacon and Edelman (*2*) have noted the presence of three sugars with R_f values less than than of sucrose in sugar sirups partially hydrolyzed by invertase.

The interfering sugar is well shown in Figure 3, sample 8, though it has run farther, in relation to raffinose, than commonly occurs.

The method, as given above, is presented as a practical, satisfactory method for large scale tests on roots of the quality normally encountered in breeding work.

Roots in abnormal condition may be encountered, which yield deionized juices unsuitable for paper chromatography because of the presence of too large an amount of colloidal matter. Such juices require a clarification step as well as the deionization treatment. The clarification step is also desirable when maximum accuracy in the raffinose determination is wished. Maximum accuracy is obtained when clarified, deionized juice is run by the upflow procedure. Upflow has not given satisfactory results on press juice treated by deionization only.

Table I. Comparison of Duplicate Tests on 204 Single Beet Roots

No. of Roots in Group	Spread in Observed % Raffinose on Sucrose
102	0
68	0.1
29	0.2
4	0.3
1	0.4

The following methods have been employed successfully for preparation of a clarified, deionized sample:

Add 0.4 to 0.5% calcium oxide on beet juice as milk of lime, heat to 80° to 85° C., add filter aid, filter on a Büchner funnel, cool, and deionize filtrate.

Clarify the juice with basic lead acetate, filter, and deionize the filtrate.

Deionize the juice sample, coagulate colloidal matter with aluminum hydrosol, and filter.

The procedures described may be applied to any beet juice or liquor, raw or defecated. On these products, where size of sample available is not a factor, deionization of a lead acetate-clarified filtrate and employment of upflow technique are recommended for greatest accuracy. Concentrations of solutions must be selected to provide a suitable quantity of raffinose in the spot placed on the paper, and standards modified to the same sucrose content and proper range of raffinose content. When products very high in raffinose content are tested, dry substance of the deionized effluent is not a satisfactory basis. Deionization is performed on a somewhat larger scale, and all samples are prepared for spotting at constant polarization. After raffinose has been determined chromatographically, its polarization is estimated and the sucrose content of the sample is taken by difference. This procedure has proved very satisfactory on molasses and saccharate sirups.

RESULTS OF TESTS ON SUGAR BEETS

It has long been observed in the Rocky Mountain area that as the campaign progresses, the raffinose content of the liquors tends to increase. The absolute value of raffinose in the liquors shows seasonal variations. The plant breeder is interested in selection of beets that will produce liquors with a minimum of raffinose. Furthermore, he is interested in the relation between raffinose in beets as harvested and the increase on storage, as beets are commonly stored for long periods before testing for selection as mothers. A few tests have been made to gain information regarding increase in raffinose during storage.

Table II. Raffinose on Sucrose in Fresh and Stored Beets

Variety No.	Mean % Raffinose on Sucrose in Roots		% Gain in Raffinose	Standard Error of Mean at Harvest
	At harvest	After 4 months' storage		
1	0.288	0.65	125	±0.027
2	0.295	0.84	185	±0.013
3	0.302	0.53	75	±0.032
4	0.330	0.78	136	±0.028
5	0.345	0.82	138	±0.017
6	0.372	0.79	112	±0.041
7	0.391	0.68	74	±0.024
8	0.432	0.82	90	±0.035
9	0.457	0.85	86	±0.036
10	0.490	0.60	22	±0.017

On October 27–28, 1950, twelve replicate samples of each of ten varieties were harvested and six replicates of each variety were tested immediately. The remaining six replicates of each variety were stored loosely in crates in a cellar at about 8° C. until February 26, 1951, a total of 4 months. On this date the various stored samples were composited to form three composites of each of the ten varieties and the 30 samples were tested for raffinose.

Table II shows the mean percentage raffinose on sucrose found in each variety at harvest time and after 4 months' storage, and the percentage increase in raffinose content in each variety.

All varieties show increases in raffinose content on storage, and although they are not constant, eight of the ten varieties show an increase of 0.4 ± 0.14% raffinose on sugar during the 4 months' storage period. All varieties lost sugar during storage, but the loss was not great enough to have a significant effect on raffinose gain. The mean loss in polarization was about 4% of the value at harvest time.

Table III. Change in Raffinose Content of Beets Stored in Outdoor Pile

Sample No.	% Raffinose on Sugar	
	Roots entering pile	Roots leaving pile
1	0.38	0.47
2	0.30	0.65
3	0.30	0.52
4	0.48	...
Mean	0.37	0.54

Data on change in raffinose on storage were obtained on a group of individual beets.

A large number of roots were harvested October 15, 1950, and stored in the cellar. On November 28, 20 roots from this group were selected at random and tested individually for raffinose content. The mean of the 20 tests showed 0.80% raffinose on sugar, and the extremes ranged from 0.53% minimum to 1.05% maximum. About January 15, 1951, raffinose tests were made on more than 200 selected roots of this same group. During this storage period of 7 weeks, the mean raffinose content increased to 1.33% on sucrose, or 0.53%. There is good reason for thinking that the raffinose content of the selected group did not differ materially from that of the mean of the whole. The individual tests on the latter group ranged from a minimum of 0.65% to a maximum of slightly above 1.5% raffinose on sucrose.

These roots, which were decidedly high in raffinose at the time of the first testing, gained raffinose on storage much more rapidly than did those of the group shown in Table II. The beets in the two series of tests were grown on fields located in two different areas.

All results thus far presented have shown extremely high percentage of raffinose on sugar. Well-developed roots grown near Denver, Colo., were dug and tested on August 1, and showed from 0.00 to 0.35% raffinose on sugar. Roots grown in the Billings, Mont., area, dug on August 14, varied from 0.1 to 0.8%, and averaged 0.54% raffinose on sugar.

In the Rocky Mountain area it is necessary to harvest all beets before a heavy freeze sets them permanently in the ground. Therefore, many beets are stored in piles which are worked out later during the campaign. While one such storage pile was being formed in the Denver area, the beets entering the pile were sampled once a week over a period of 4 weeks, during which the pile was being formed. The pile was taken out during a 3-day period, after an average storage period of about 9 weeks. At the time the pile was taken out, the roots were carefully sampled.

The results of the tests for raffinose on the beets entering and leaving the pile are given in Table III.

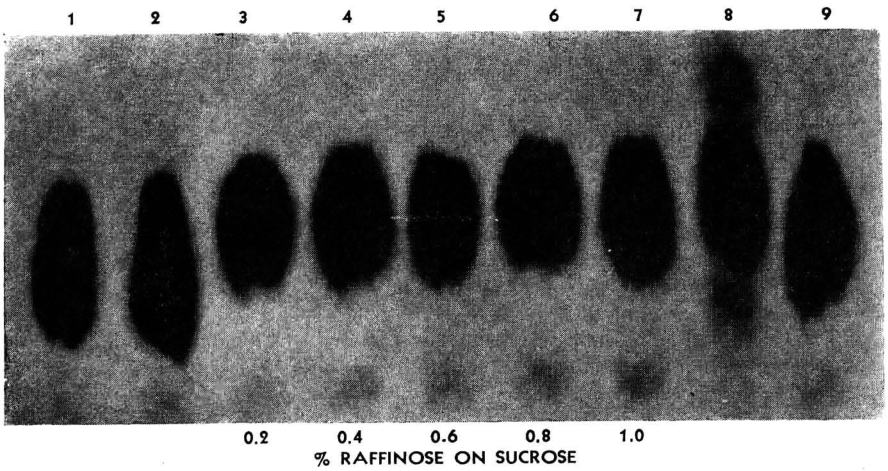

Figure 3. Finished Chromatogram of Beet Juices and Raffinose Standards

The results show an increase in raffinose during storage in the pile, but the rate of increase is much less than in roots stored in the cellar.

DISCUSSION

That the raffinose content of sugar beets increases during storage appears to be demonstrated without question, but it is too early to attempt an authoritative discussion of the factors which determine the absolute level of raffinose in the roots at harvest time or the rate at which the raffinose content increases during storage. Environmental factors during the growth of the beet may be of major importance. Heredity appears to be a factor. Much additional information is needed on the whole subject.

The quantities of raffinose found in most beets tested during the past season were far above the expected value. However, it has been demonstrated that the quantities of certain other components may differ widely between beets grown on average commercial fields and beets grown on highly fertile experimental fields, and since only the results given in Table III were obtained on commercially grown beets, it is possible that the data presented herein may tend to create a false impression of the normal raffinose content of commercial beets. Most of the beets encountered in the present investigation were far above the normal for commercial beets of the Rocky Mountain area.

As a check on the above observation, press juice was obtained from a large batch of pulp from the same group of beets considered in Table I (average, 1.33% raffinose on sugar). The press juice was given the standard lime defecation and carbonation treatments, and a pan was boiled from the juice in order to produce a green sirup in which the raffinose content would be sufficiently great to ensure accuracy of the raffinose determination by invertase and melibiase hydrolysis. The green sirup showed 82.6% sucrose and 2.25% raffinose on dry substance, equivalent to 13% raffinose on impurities. On further crystallization of sugar, this raffinose would be found in the molasses at the same per cent on molasses impurities. The average raffinose content of molasses from beets in the Great Western Sugar Co. area in 1950 was about 4.5% on impurities.

While the mother beets that were tested averaged abnormally high in raffinose content, a few of relatively low raffinose content were found, and possibly the plant breeders may develop a strain of low raffinose beets from those few.

ACKNOWLEDGMENT

The writer is indebted to numerous persons for assistance in this investigation. First, he gives his thanks to H. C. S. deWhalley, director of the Tate and Lyle Research Laboratories, for information, in advance of publication, on his work on the determination of raffinose in raw beet sugars. Various members of the staffs of the Research Laboratory and the Experiment Station of the Great Western Sugar have given valuable assistance, especially Ralph Wood.

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Determination of Geometric Surface Area of Crushed Porous Solids

Gas Flow Method

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DETERMINATION of specific surface area of solids has long been the subject of numerous investigations in connection with correlating the energy spent in crushing with new surface created. Although the establishment of such a relationship would be of great practical use to the process industries of crushing, the interest in surface determination has by no means been limited to crushing. Surface determinations are generally a means to an end—i.e., the knowledge of surface in itself is not so important as the application of such knowledge to estimation of reaction, heat and mass transfer rates, and pressure drop, and to numerous processes in industrial operations.

Most solids possess, in addition to their external visible surface, an internal surface due to existence of empty spaces within their boundaries. If these internal spaces are considerably larger than molecular sizes, they are referred to as pores, and the material is spoken of as being porous. Differentiation between the external surface and the internal surface of porous particles is often important, but is difficult to make, as there exists no definite boundary between them.

A geometric surface, as distinct from external surface, may be visualized as the surface of an impervious envelope surrounding the body in an aerodynamic sense. Irregularities and striae on the surface would not be taken into account in a geometric surface in contrast to external surface. Whether the value of the internal, or the external, or the geometric surface area is desired will depend on the objective. Geometric surface areas are required in connection with sedimentation rates, resistance to the flow of fluids, bulk density and packing problems, and heat and mass transfer rates in flow processes. If rates of solution and reaction, and hygroscopic or total adsorptive properties are in question, the total accessible area is the relevant area.

Diversified interests in surface area measurements have led to the development of various methods, and in recent years the literature on the subject has grown rapidly. Dissolution methods developed by Wolff (*83*), and Martin and coworkers (*70*), and later extended by Schelte (*76*) and Gross and Zimmerley (*38*), have been used to measure surface areas of glass beads, crushed quartz, etc. These methods, however, are limited to materials for which a suitable solvent exists; even then critics have regarded the method as doubtful (*3*, *74*).

The proportionality of heat of wetting for a given solid-liquid pair to the surface area of the solid has been utilized by various

Particles of crushed porous solids possess a geometric surface—the surface of an impervious envelope surrounding the particles in an aerodynamic sense. Knowledge of geometric surface areas is essential to solving problems arising from gas flow through beds of solids, and no satisfactory method has existed for crushed porous solids. A gas flow method is described that permits determination of the geometric surface areas of crushed porous solids from the measurements of pressure drop as a function of gas flow rates and bulk densities. The method, which is based on a fundamental flow equation, automatically determines the particle density of the porous solids and offers two alternative methods of mathematical analyses. The equation employed in one of the methods is entirely new in this field. Results are reported for numerous cokes of different origin as well as mesh sizes. Geometric surface areas are essential in the estimation of rates of sedimentation, resistance to flow of fluids, bulk density and packing problems, and rates of heat and mass transfer in flow processes. For example, in the passage of appreciable quantities of gas through beds made up of porous solids, the flow, in effect, surrounds the particles, the gas almost entirely passing through the void space, and the pressure loss, heat, and mass transfer rates accompanying the flow are a function of both the surface surrounded and the void space. The method also determines void space as a result of the measurement of particle density.

workers (*8, 13, 14, 37, 39, 57*) to determine the surface area of powders. Gregg (*37*) regarded heat of wetting methods as free from uncertainties if the specific heat of wetting for the solid-liquid pair in question is known. The area measured, however, is necessarily that of the surface accessible to the molecules of the wetting liquid.

Adsorption of dyes (*62, 73, 76*), radioactive substances (*73*), and various other solutes from solution (*34, 37, 49*), has been perhaps the most widely used method on account of of its relative experimental ease. The method, however, cannot be used for the absolute determination of the total surface area of porous powders. Uncertainties regarding the relative adsorption of solvent and solute, and also the orientation of the solute molecules on the adsorbent surface, render the method doubtful. The area measured, as in the case of heat of wetting method, is that of the surface accessible to the molecules of adsorbate. If a knowledge of external area is desired, the molecules of the adsorbate should be large enough so that they do not penetrate the pores.

Recent advances in gas adsorption theories, with the development of the Brunauer, Emmett, and Teller (*17*) and Harkins and Jura (*39–41, 53, 54*) methods, have attracted wide interest; and gas adsorption methods have been used widely for determination of total surface area of solids (*2, 7, 9–12, 15, 16, 18, 24–28, 35, 37, 44, 50, 51, 57, 59, 67, 71, 84–86*). Adsorption methods in general depend on the evaluation of the monolayer capacity of the solids. For solids having extremely fine pores, however, capillary condensation greatly affects the course of the isothermal adsorption curves and, in many instances, may account for nearly all of the adsorption. Kistler, Fischer, and Freeman (*58*) have utilized the Boltzmann equation relating the capillary condensation to relative pressure and surface tension to develop an equation that permits evaluation of the total surface area from an adsorption isotherm. Other treatments base their origin on the Kelvin equation relating the capillary radii to vapor pressure of the liquid condensed. Early attempts are due to Lowry and Hulett (*69*), Foster (*32*), and Lowry (*68*). Based on the same principle, Harvey (*42*) outlined a method for obtaining the surface area of a large volume of pores distributed over a wide range of radii with the use of adsorption isotherms.

Surface estimation methods based on size analysis by sieving, elutriation, sedimentation, centrifugal sedimentation, etc. (*3, 43, 45–47, 74*), aim to establish a shape factor or volume and surface factors which would enable calculation of specific surface when the characteristic dimension is determined by the particular method of size analysis. These methods are based on statistical processes by which size segregation is effected. Size analyses by ordinary or electron microscope measurements (*2, 33, 43, 55, 62, 81, 82*) differ from those mentioned above in that the particles are measured individually instead of being grouped statistically by some process of classification. There remains the problem of obtaining a representative sample which may involve a large number of particles if there is a great variation in size. The position in which the particles rest when distributed on a slide introduces uncertainties in that the particles will not rest in all random positions, but only in stable positions.

Photometric or light-extinction methods (*33, 45, 52, 77, 78*) are based on the absorption of light by solid particles dispersed uniformly in a fluid medium. These methods, like the microscopic one, measure the projected area of the particles, but unlike the microscopic methods, they yield the projection area in all random positions. Calculation of the surface area is based on a relationship set forth by Cauchy (*22*), who has shown that for irregular solids randomly oriented in all positions, the geometric surface area is four times the average projection area. Size analyses and photometric methods necessarily measure the geometric surface area unless corrected empirically by factors accounting for surface roughness.

Permeability or fluid flow methods are used extensively for determination of specific surface of powders on account of the simple apparatus required. The principle of the methods is the use of a flow equation to determine the specific surface from measurements of flow rate and pressure drop. Permeability methods owe their widespread use to the development of the Kozeny equation (*19, 60, 63, 64*). The Kozeny equation is based on the Poiseuille flow and has been found to be satisfactory at low rates of gas flow through beds of particles having specific surfaces less than 2000 sq. cm. per cc. (*1, 12, 13, 36, 61, 75, 79, 80*). Through extremely fine material whose dimensions are comparable to the mean free path of the gas, diffusion or molecular flow must be taken into account. Rigden (*75*), Keyes (*56*), Arnell (*4, 5*), Lea and Nurse (*63*), Carman (*21*), and others have modified the Kozeny equation to include terms that account for the molecular flow, while Holmes (*48*) and later Deryagin *et al.* (*23*) have developed flow equations based on Knudsen's law for gas diffusion through a fine channel. While these modifications stemmed from the investigation of the validity of the Kozeny equation at extremely low rates of gas flow through fine powders, studies on coarser material at the higher rates (*20, 31, 65, 66, 72*) have shown great departure from the Kozeny equation.

The validity of the results of the specific surface determinations by the use of flow methods depends upon the validity of the flow equation used. Accepting, for the moment, the validity of any one of the flow equations, an additional problem presents itself—i.e., determination of the fractional void volume, one of the important variables in the flow equations, offers difficulty in the case of crushed porous solids. The fractional void volume is calculated from the bulk density of the packing and the particle density of the solids, the latter of which is not usually known and which is not a characteristic property because it changes with particle size. Therefore, determination of the specific surface of porous solids by gas flow methods hinges upon a determination of the particle density of the material, as well as the validity of the flow equation used. For this reason the present paper was preceded by two articles—one on the development of a flow equation in the flow of fluids through granular beds (*30*), the other on the determination of the particle density of crushed porous solids (*29*). Consequently, it has been possible to develop methods whereby the specific surface of crushed porous solids can be determined by gas flow methods. The flow equation developed is for beds having specific surfaces less than 2000 sq. cm. per cc. This roughly corresponds to particles larger than 0.1 mm. in size or +140-mesh. Therefore, the method to be developed must necessarily be limited to particles larger than 0.1 mm. (for fine powders cf. *4, 5, 21, 56, 63, 75*).

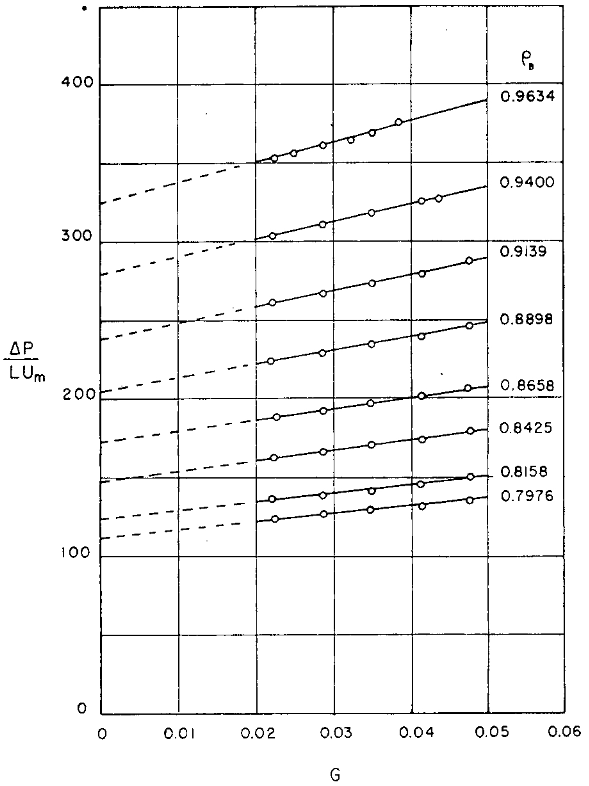

Figure 1. Typical Plots of Equation 1 for a System Packed to Different Fractional Void Volumes

Nitrogen flow through 40- to 60-mesh high temperature oven coke (sample 8). Cross-sectional area of tube 7.24 sq. cm. P/LU_m is in dynes sec./cm.^{4} or in grams/sec. cc. and G is in grams/sec. sq. cm. Lines drawn according to method of least squares

THEORETICAL

In a bed, particles of porous material may be visualized aerodynamically as surrounded individually by impervious envelopes. The weight per unit of enveloped volume may be defined as the particle density, which is often referred to as the apparent density, and the area of the enveloping surfaces per unit of enveloped volume as the specific surface. Under these conditions the void volume is conceived of as the space between the enveloped particles. In the passage of appreciable quantities of gas through beds made up of porous solids, the flow, in effect, surrounds the particles, and the gas almost entirely passes through the void space. As the pressure loss accompanying the flow is a function of both the surface surrounded and the void space, its measurement should lead to the determination of the surface and the void volume.

The theoretical considerations and the experimental data led to the development of the following linear expression for pressure drop through granular beds (*30*).

$$\Delta P/LU_m = a + bG \tag{1}$$

where ΔP is the pressure drop, L is the height of the bed, U_m is the average linear gas velocity based on the cross section of the empty column, G is the mass flow rate per unit area of the cross section, and a and b are coefficients which are represented by

$$a = k_1 \mu S_v^2 \frac{(1 - \epsilon)^2}{\epsilon^3} \tag{2}$$

$$b = k_2 S_v \frac{(1 - \epsilon)}{\epsilon^3} \tag{3}$$

where μ represents the absolute viscosity of the gas, S_v the specific surface area of the particles, ϵ the fractional void volume of the bed, and k_1 and k_2 are numerical constants. When the ratios of pressure gradient to average velocity are plotted against mass flow rate according to Equation 1, a straight line is obtained (Figure 1) having the intercept a and the slope b. To determine the specific surface from either the slope or the intercept, it is necessary to know the fractional void volume. The fractional void volume can be obtained from a knowledge of the bulk density of the solids in the bed and the particle density of the solids by the use of the following relationship:

$$\epsilon = 1 - \frac{\rho_B}{\rho} \tag{4}$$

where ρ_B is the bulk density and ρ is the particle density. Substitution of Equation 4 into Equations 2 and 3 and solving for S_v will yield

$$S_v = \sqrt{\frac{a}{k_1 \mu} \frac{(\rho - \rho_B)^3}{\rho \rho_B^2}} \tag{5}$$

and

$$S_v = \frac{b}{k_2} \frac{(\rho - \rho_B)^3}{\rho^2 \rho_B} \tag{6}$$

Table I. Specific Surface Determinations for High Temperature Coke

Sieve Size U. S. Standard	Particle Density, G./Cc.	Specific Surface, Cm.$^{-1}$	
		Eq. 7	Eq. 8
8–16	0.92	32	28
16–20	1.07	68	64
20–30	1.15	103	99
30–40	1.23	150	150
40–50	1.30	200	220
50–60	1.47	330	360
60–80	1.55	440	...
80–100	1.58	530	...
100–140	1.59	800	...

If the particle density of the material is known, the specific surface can be calculated by the use of either equation from a single plot of $\Delta P/LU_m$ *vs.* G. For the pulverized porous material, however, the particle density is unknown, and must necessarily be determined. In this respect the method to be described is self-determining. Equations 5 and 6 can be transformed into the following respective forms:

$$\rho_B = \rho - (k_1 \mu S_v^2 \rho)^{1/3} (\rho_B^2/a)^{1/3} \tag{7}$$

Table II. Specific Surface Determinations for Various Cokes

(40-60 mesh size)

Sample No.	Particle Density, G./Cc.	Specific Surface, Cm.$^{-1}$		Specific Surface, Sq. Cm./G.
		Intercept	Slope	
1	1.41	300	330	210
2	1.40	250	250	180
3	1.52	310	330	200
4	1.56	340	360	220
5	1.43	240	220	170
6	1.53	270	290	180
7	1.56	260	250	170
8	1.56	260	250	170
9	1.57	280	310	180
10	1.36	290	280	210
11	1.41	330	350	230
12	1.29	260	290	200
13	1.33	320	320	240
14	1.49	310	310	210
15	1.46	270	270	190
16	1.19	280	280	220
17	1.21	290	290	240
18	1.19	270	270	230
19	1.24	320	350	260
20	1.22	280	280	230
21	1.17	290	280	250
22	1.28	330	360	260
23	1.46	260	290	180

and

$$\rho_B = \rho - (k_2 S_v \rho^2)^{1/3} (\rho_B / b)^{1/3} \tag{8}$$

The essence of the procedures to be followed is to measure pressure drops as a function of gas flow rates at different bulk densities to which a known amount of the solids can be packed, and to determine the values of *a* and *b* by a plot of $\Delta P/LU_m$ *vs.* G (Equation 1) by the use of the method of least squares. For each bulk density a different set of values of *a* and *b* will be obtained. According to Equations 7 and 8 the only variables involved in the procedure are ρ_B and *a* and *b;* therefore, ρ_B will be linear with respect to $\left(\frac{\rho_B^2}{a}\right)^{1/3}$ and to $\left(\frac{\rho_B}{b}\right)^{1/3}$ in the corresponding equations. Consequently the graphical representation of both Equations 7 and 8 will yield the particle density as the intercept and $\sqrt[3]{k_1 \mu S_v^2 \rho}$ and $\sqrt[3]{k_2 S_v \rho^2}$, respectively, as the slope. Once the slopes and the intercept are determined, S_B can be obtained from either slope. Accordingly, the method offers two alternative procedures—the use of Equation 7 and the use of Equation 8.

EXPERIMENTAL

The apparatus has been described in detail (*29*). It consisted of a glass column fitted with a porous disk, flowmeters, and manometers. The procedure involved the introduction of a known weight of pulverized porous material into the tube, packing the solids into various bulk densities, and measuring the pressure loss through each packing as a function of nitrogen flow rate. Packing of a given amount of solids into different bulk densities was effected by partial fluidization of the solids (for further details see *29*).

DISCUSSION

In the preceding paper (*29*), the above equations were introduced for the purpose of determining the particle density of crushed porous solids. The validity of the methods was checked with nonporous solids by comparing the results with water displacement densities. The agreement was good. Upon inspection of Equation 1 it is seen that as the flow rate approaches zero as a limit, the $\Delta P/LU_m$ term will equal coefficient *a*. Under these conditions, the equation is identical with the classical Kozeny equation. In a recent study of the flow of an air stream through a layer of granules, Arthur and coworkers (*6*) transformed the Kozeny equation into a form similar to that of Equation 7. The authors observed that in order for the relation to be true, its graphical representation should be linear, and the intercept and the slope should lead to the values of the particle density and the specific surface. The method was used in the determination of specific surface. It is, however, not applicable to coarser particles at the higher flow rates, as the Kozeny equation is valid only for gas velocities approaching zero.

The distinctive features of the present method are: It is based on a fundamental general flow equation valid at all flow rates; it automatically determines the particle density of the solids; and it offers two alternative procedures—viz., Equations 7 and 8. Whereas the original form of Equation 7—i.e., Equation 2—is identical in form with the Kozeny equation and as such is not novel in specific surface determinations, Equation 8 and its original form, Equation 3, are entirely new for this purpose. Besides its novelty, Equation 8 is the only equation developed thus far that permits determination of surface area by gas flow for particles larger than 2.5 mm. Its applicability has been demonstrated with beds composed of coke +50 mm. in size.

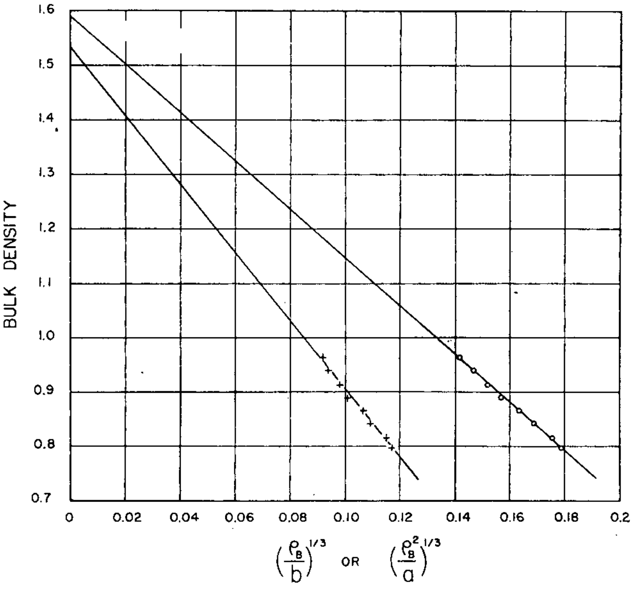

Figure 2. Graphical Representations of Equations 7 and 8

Data from Figure 1 are used. Solid lines drawn by method of least squares

The selection between Equations 7 and 8 should be based upon a calculation of the probable error for coefficients *a* and *b* of Equation 1. In general, *a* will be more accurate for smaller sized particles and at lower flow rates, and *b* for larger sized particles and at higher flow rates. Depending upon the flow rates employed, however, there will be a size range where both equations can be used effectively. In the present investigation, when superficial gas velocities of 3 to 45 cm. per sec. are employed, this overlapping size range has been found to lie between 0.18 and 2.4 mm. Inasmuch as the graphical representations of Equations 7 and 8 lead to the value of particle density, one method can serve as a check for the other. When separate regression lines based on these two equations were drawn, in no case did the intercept of one equation fall outside the specified error range of the intercept of the other equation. A special method of least squares (see calculations below), therefore, was developed which results in two regression lines with a common intercept. The method in principle is based on minimizing the sum of the squared deviations of both regression equations simultaneously.

A typical plot of Equation 1 is shown in Figure 1. The intercept and slopes of Figure 1 obtained by the method of least squares are represented graphically in Figure 2 according to Equations 7 and 8, respectively. The solid lines are again drawn by the method of least squares. It is seen that Equation 7 leads to a value of 1.57 grams per cc. for the particle density, whereas Equation 8 leads to 1.53. The experimental results on 32 samples of cokes did not show any deviation over 3%. In most experiments identical results were obtained. Figure 3 shows the regression lines when drawn according to the special method of least squares described below for the same data presented in Figure 2. In every case the common intercept obtained by the special method fell within a region formed by the overlapping of the specified error ranges about the separate intercepts of Equations 7 and 8.

The value of the particle density determined by this method is absolute in that it is calculated from the quantities measured directly. The value of the geometric surface area, however, is not. S_v will depend upon the value chosen for k_1 and/or k_2. The experiments with solids of known surface areas and densities, e.g., spheres, cylinders, nodules, tablets, etc., resulted in the value 4.2 for k_1 and 0.292 for k_2 (*30*), but substitution of these values in Equations 7 and 8 gave different results for S_v. [The actual figures reported in the article are 150 ($\approx 36 \times 4.2$) and 1.75 ($\approx 6 \times 0.292$) on account of the substitution of the equivalent particle diameter in place of specific surface.]

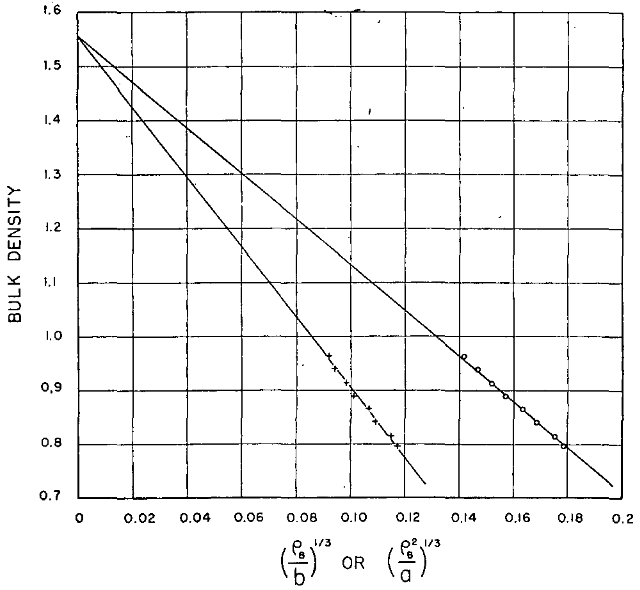

Figure 3. Graphical Representations of Equations 7 and 8

Data from Figure 1 are used. Solid lines with common intercept drawn according to method of least squares described in Calculations

Nothing that has been done here or is available in the literature enables the determination of the exact values that should be used for k_1 and k_2 for crushed porous solids. The constant k_1 is identical with the Kozeny constant, to which values ranging from 3.1 to 5.0 have been assigned (*4*). As the value 4.2 for k_1 was within this range, and the standard error of estimate gave a smaller percentage error for k_1 than k_2 in the above instance, 4.2 was adopted for k_1 and k_2 was corrected to 0.48 to yield comparable results for the porous materials studied.

The results of the application of the above method to cokes are listed in Tables I and II. The specific surfaces of the various samples calculated by the two alternative equations show good agreement: The average deviation between the two is about ±4%. As no other independent method of determining the specific surface area of the cokes was available, the results cannot be checked, but judging from the sieve size, they are reasonable.

CALCULATIONS

The equations for two straight lines with negative slopes and a common positive intercept at the y axis are given by:

$$y = A - Bx \tag{A-1}$$

$$y = A - Cz \tag{A-2}$$

The deviations of the experimental results from the linear relationships are:

$$\Delta = A - Bx - y \tag{A-3}$$

$$\Delta' = A - Cz - y \tag{A-4}$$

where y, x, and z are the observed values.

By holding $\Sigma\Delta^2$ and $\Sigma\Delta'^2$ at minimum, two independent regression lines will result. However, keeping $(\Sigma\Delta^2 + \Sigma\Delta'^2)$ at a minimum will yield two regression lines with a common intercept. In order for $(\Sigma\Delta^2 + \Sigma\Delta'^2)$ to be minimum it is required that

$$\frac{\partial}{\partial A}\Sigma(\Delta^2 + \Delta'^2) = 0 \tag{A-5}$$

$$\frac{\partial}{\partial B}\Sigma(\Delta^2 + \Delta'^2) = 0 \tag{A-6}$$

$$\frac{\partial}{\partial C}\Sigma(\Delta^2 + \Delta'^2) = 0 \tag{A-7}$$

Since $\frac{\partial\Delta^2}{\partial A} = 2\Delta, \frac{\partial\Delta'^2}{\partial A} = 2\Delta', \frac{\partial\Delta^2}{\partial B} = -2x\Delta, \frac{\partial\Delta'^2}{\partial B} = 0, \frac{\partial\Delta^2}{\partial C} = 0,$ and $\frac{\partial\Delta'^2}{\partial C} = -2z\Delta'$, it follows that

$$\Sigma(\Delta + \Delta') = 0 \tag{A-8}$$

$$\Sigma x\Delta = 0 \tag{A-9}$$

$$\Sigma z\Delta' = 0 \tag{A-10}$$

Substitution of Δ and Δ' in Equations A-3 and A-4 into A-8, A-9, and A-10 leads to

$$A = \frac{1}{n}\Sigma y + \frac{1}{2n}B\Sigma x + \frac{1}{2n}C\Sigma z \tag{A-11}$$

$$A\Sigma x - B\Sigma x^2 - \Sigma xy = 0 \tag{A-12}$$

$$A\Sigma z - C\Sigma z^2 - \Sigma zy = 0 \tag{A-13}$$

where n is the number of experiments. Substituting $\bar{y}$, $\bar{x}$, and $\bar{z}$ for $\frac{1}{n}\Sigma y$, $\frac{1}{n}\Sigma x$, and $\frac{1}{n}\Sigma z$, respectively, and solving for A, B, and C,

$$A = \bar{y} + \frac{1}{2}\bar{x}B + \frac{1}{2}\bar{z}C \tag{A-14}$$

$$B = \frac{\left(\bar{y}\Sigma z^2 - \frac{1}{2}\bar{z}\Sigma zy\right)\Sigma x - \left(\Sigma z^2 - \frac{1}{2}\bar{z}\Sigma z\right)\Sigma xy}{(\Sigma x^2)(\Sigma z^2) - \frac{1}{2}\bar{x}(\Sigma x)(\Sigma z^2) - \frac{1}{2}\bar{z}(\Sigma z)(\Sigma x^2)} \tag{A-15}$$

$$C = \frac{\left(\bar{y}\Sigma x^2 - \frac{1}{2}\bar{x}\Sigma xy\right)\Sigma z - \left(\Sigma x^2 - \frac{1}{2}\bar{x}\Sigma x\right)\Sigma zy}{(\Sigma x^2)(\Sigma z^2) - \frac{1}{2}\bar{x}(\Sigma x)(\Sigma z^2) - \frac{1}{2}\bar{z}(\Sigma z)(\Sigma x^2)} \tag{A-16}$$

If we denote $\rho_B = y$, $\sqrt[3]{\frac{\rho_B^2}{a}} = x$, and $\sqrt[3]{\frac{\rho_B}{b}} = z$ in Equations 7 and 8, then

$$\rho = A \tag{A-17}$$

$$\sqrt[3]{4.2\mu S_v^2\rho} = B \tag{A-18}$$

$$\sqrt[3]{0.48S_v\rho^2} = C \tag{A-19}$$

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Correction

The second sentence in a paper on the "Coulometric Titration of Vanadium" [Anal. Chem., **23**, 1665 (1951)], although intended to deal with the estimation of vanadium with ferrous ion, might be interpreted to imply that no prior work had been done on the coulometric estimation of vanadium. Such work has been done with cuprous ion by D. J. Meier, R. J. Myers, and E. H. Swift [*J. Am. Chem. Soc.*, **71**, 2340 (1949)].

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Precision of a Simple Flame Photometer

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To improve the ease and accuracy of sodium and potassium determinations in biological samples, a simple flame photometer has been built employing glass and interference filters, photovoltaic cells, and a galvanometer. Its air-gas flame is completely enclosed to prevent atmospheric contamination. With well-regulated gas and compressed air supplies, average departures from the average of thirty successive readings of ±1% were measured for direct intensities and ±0.3% for internal standard readings. With unregulated gas pressure and less careful air pressure regulation, the average departure for the internal standard measurements increased to ±0.5%. The readings were least affected by gas pressure changes with a large flame burning relatively little primary air. Their stability with respect to air pressure changes was constant over a wide range of conditions. The accuracy obtainable permits the measurement of the small changes in concentration that are significant when the normal range is only a small fraction of the amount present, as in the case of sodium in serum.

THE most useful applications of flame photometry are in determinations of the alkali metals, which are easiest by this method and most difficult by chemical procedures. Photoelectric flame photometers suitable for such analyses have been described by Barnes *et al.* (*1*), Berry *et al.* (*2*), Bowman and Berliner (*4*), Fox (*5*), Gilbert *et al.* (*6*), Schuhknecht (*8*), Weichselbaum and Varney (*9*), and others. A number of these instruments are now commercially obtainable. The instrumentation has been developed to the point where flame photometry is suitable for use in many chemical as well as spectrographic laboratories. However, for medical applications there is still need for greater simplicity, so that reliable analyses may be made by relatively unskilled operators. In addition, the accuracy required in determinations such as sodium in blood serum is sometimes not attainable. In the instrument described the range is restricted to sodium, potassium, and, in some cases, calcium, which permits the use of such simple designs and controls that accidental errors are greatly reduced.

The accuracy of the flame photometric method has been reported in a number of papers, the most comprehensive being those of Berry, Parks *et al.* (*7*), Bills *et al.* (*3*), and Fox. They have reported accuracies of ±1% of the amount present in the determination of sodium and potassium, using instruments in which the atomizer is separate from the burner. Weichselbaum and Gilbert have reported accuracies of a few tenths of 1% when the sample is atomized directly into the flame. This paper describes a very simple instrument of the former type and discusses its stability and precision.

The only factors affecting stability that are considered are air pressure, gas pressure, and burner adjustment, the ones that affect the reproducibility of repeat measurements of the same sample. These set a limit to the analytical accuracy obtainable from the instrument. By the use of suitable precautions and calibrations, this accuracy may be approached but not exceeded. The effects of such variations as viscosity, pH, surface tension, etc., are not considered. They are reported in the references above along with a summary of the literature on the accuracy of flame photometry.

ATOMIZER AND BURNER

The atomizer and the burner system are shown schematically in Figure 1.

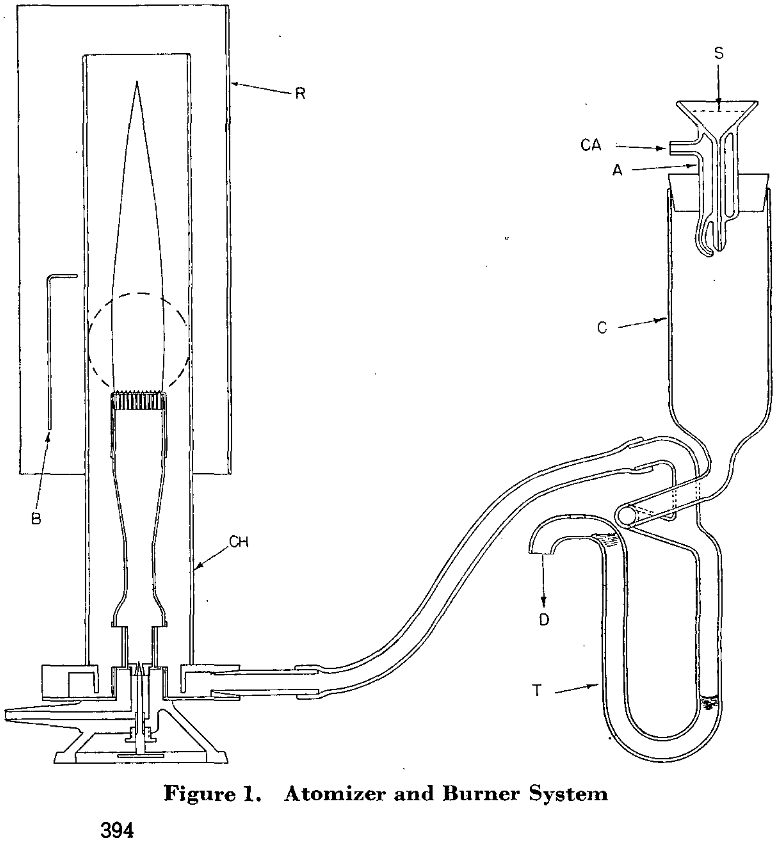

Figure 1. Atomizer and Burner System

The glass atomizer, *A*, is held in the center of a large glass chamber, *C*. Sample *S* is introduced through the funnel in the top of the atomizer and compressed air through the inlet, *CA*. The atomizer uses about 2.5 cubic feet per minute of compressed air at 9 pounds per square inch and consumes 4 cc. of sample per minute under these conditions. Its sample tube is 0.3 mm. in inside diameter with no constriction anywhere along its length. The absence of a constriction is important in avoiding plugging of the capillary by dirt and dust. In addition, the capillary is straight, so that any dirt lodging there is readily pushed through.

The atomized sample blows down through a chamber 1.62 inches in inside diameter and 5 inches long. At the bottom the fine fog is separated from the larger drops of liquid in a loop of 0.5 inch tubing. The fog goes out to the burner, and the unused liquid goes through a liquid trap, *T*, to the drain, *D*. There is an opening in the tubing following the liquid trap to avoid siphoning the liquid out of the trap.

The burner is a standard Fisher Type 3-900 for burning city gas, modified for some of the experiments to take various fixed-diameter gas jets instead of its original variable orifice. Its throat area is 0.31 square inch, its grid area, 0.57 square inch, and its maximum air inlet area, 0.94 square inch. The fixed gas jets used had diameters of 0.052, 0.070, 0.082, and 0.100 inch. The burner is surrounded by a 2-inch glass chimney, *CH*, 12 inches long.

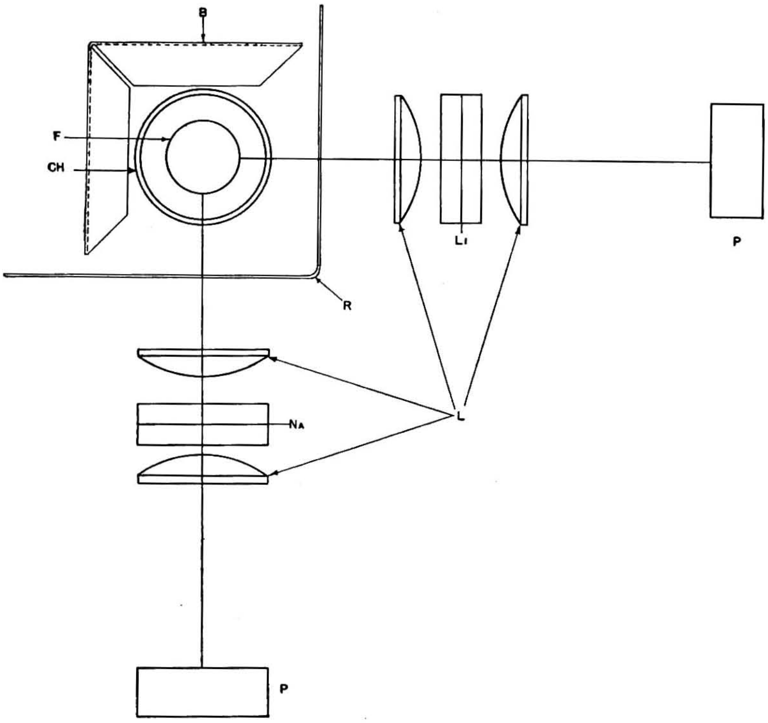

Figure 2. Optical System

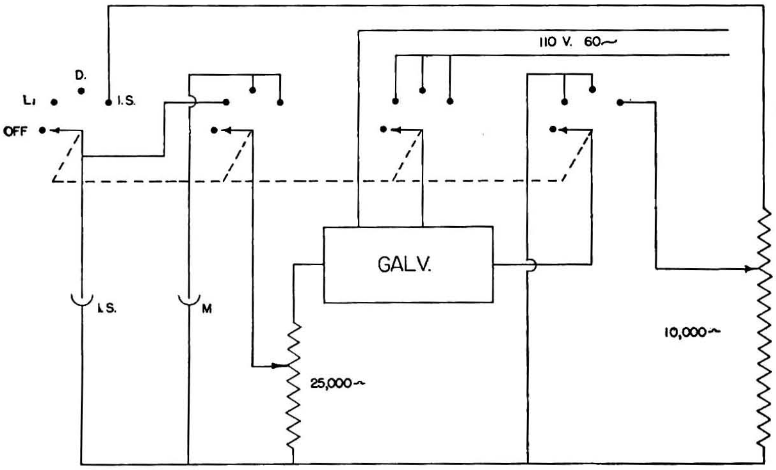

Figure 3. Schematic Wiring Diagram

Air containing atomized sample enters past a baffle into the space inside the chimney. As there is no opening to the atmosphere at the base of the chimney, all the air supply to the burner is obtained from the atomizer, and there is no possibility that smoky or dust-bearing room air will get into the flame. Sample is introduced into the flame both in the primary air drawn in at the bottom of the burner and in the secondary air at the top.

The chimney also reduces heat conduction and convection from the flame to the body of the instrument. To reduce heating still further, a bright aluminum reflector, *R*, keeps most of the radiant energy out of the instrument. Two openings provide paths for the light beams to reach the photocells. The photocells look through them and the flame into a black light trap, *B*. The trap becomes hot and must be insulated from the reflector.

For the most stable operation the air supply to the atomizer was regulated by two diaphragm regulators connected into the line in series. The gas supply had a normal pressure of about 9 inches of water and a fuel value of 528 B.t.u. per cubic foot. It was regulated by passing through an adjustable constriction to the burner and to another tube immersed an adjustable distance below a water surface, thus stabilizing the pressure at the burner whenever part of the flow escaped through the bubbler tube.

OPTICAL SYSTEM

The optical system is shown in Figure 2.

Two beams of light are taken from the flame just above the top of the burner. Each light path has two condensing lenses, *L*, of 2-inch diameter and 3-inch focal length, which focus images of the lower part of the flame, *F*, on the photocells, *P*.

The filters for isolating different emission lines are located between the lenses. The lithium filter, *Li*, is positioned in the internal standard beam, while the other filters, *Na*, are held on a rotating plate so arranged that any other filter may be inserted into the other beam. For measurements of lithium concentrations, the lithium photocell is switched into the part of the circuit normally occupied by the other photocell.

The combinations of filters selected for the determination of the different elements are given in Table I. Those marked I are simple filters for general use. Those marked II are more complicated and expensive filters for the determination of small amounts of unknowns in the presence of large amounts of interfering elements.

ELECTRICAL SYSTEM

The schematic wiring diagram in Figure 3 shows a simple potentiometer circuit with a single sensitivity control and one switch to shift from internal standard to lithium and to direct intensity measurement of other elements.

The internal standard potentiometer for balancing the amount of unknown light against the lithium light is a 10,000-ohm Beckman helipot. With a ten-turn duodial, it gives an internal standard scale 1000 divisions long. The photocells are of the self-generating type (Vickers Electric Division, Vickers, Inc., 1815 Locust St., St. Louis, Mo.).

Table I. Filter Data

For each filter are given the components, transmittance to the desired radiation, minimum detectable concentration in parts per million, and the interference factors expressed as the relative gravimetric concentrations of the interfering and desired elements needed to produce the same signal.

Filter	K	Na I	Li I	Ca I	Na II	Li II	Ca II
Components	C-2600	C-3480 C-9780	C-2403 B-6708	C-5120 C-2412 CB-ON20 CB-ON20	C-3480 C-9788 B-5893	C-2403 B-6708 B-6708	C-2412 C-5120 B-6240 CB-ON20
Transmittance, %	75	18	55	25	18	35	15
Minimum detectable	0.05	0.05	0.3	1	0.05	0.5	2
Interference factor							
K	..	3000	40	4	3000	2000	10
Na	9000	..	3000	100	..	3000	200
Li	9000	3000	..	1	3000	..	30
Ca	9000	100	400	..	600	1000	..

C. Glass filter from Corning Glass Works, Corning, N. Y.
B. Dielectric interference filter from Baird Associates, Inc., Cambridge, Mass.
CB. Glass filter from Chance Brothers, Ltd., Glass Works, Smethwick 40, Birmingham, England.

The galvanometer is a General Electric (General Electric Co., Schenectady, N. Y.) high-sensitivity portable Type 32C-246G13. Its characteristics are: sensitivity, 0.0007 microampere per mm.; resistance, 1900 ohms; external critical damping resistance, 42,000 ohms; period, 4 seconds. It is used with less than its critical damping resistance to increase the current output from the photocell and hence to increase the deflection for a given concentration of unknown. The speed of response of the complete flame photometer is limited by the time needed to flush out the atomizer chamber, which is about 20 seconds. The increase in the galvanometer's response time by overdamping is not important, so long as it is much smaller than this.

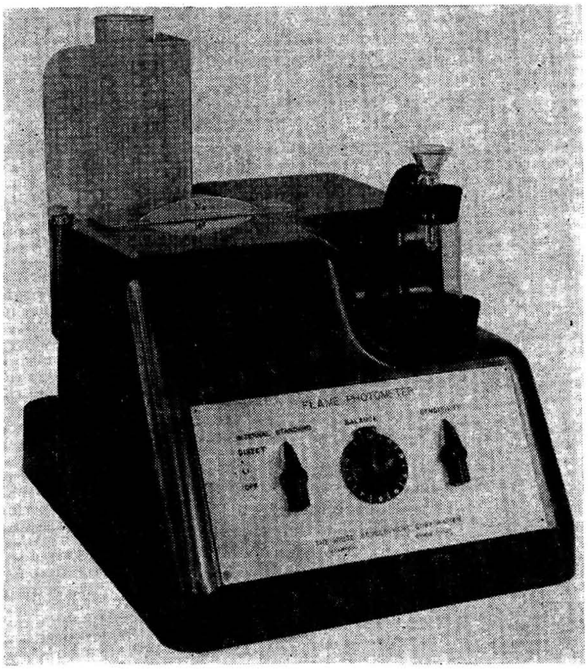

Figure 4. Flame Photometer

Figure 4 is a photograph of the flame photometer.

The main housing is an aluminum casting. The atomizer and atomizer chamber project out of the front right-hand corner. The burner is diagonally opposite in the back, hidden from view by the reflector. The optical system is just below the top with the lithium photocell behind the atomizer and the other to the left of it. The control panel on the front includes the three electrical controls. The remaining operating control is the element selector wheel, which projects through the top and has different filters mounted on it.

PERFORMANCE

The flame photometer has been set up and operated in several laboratories over a period of 8 months. It has shown unusual stability and freedom from atmospheric contamination. Accurate determinations of sodium and potassium are possible in smoky or dusty rooms. The atomizer seldom clogs. For low concentrations the noise level is less than half a galvanometer division. However, because this is about the limit of readability, it is arbitrarily assumed to be the minimum detectable signal. The corresponding minimum detectable concentrations given in Table I were calculated from the deflections measured for four solutions containing 200 p.p.m. of calcium, and 10 p.p.m. of sodium, potassium, and lithium, respectively.

Figure 5 shows direct and internal standard calibration curves for sodium; Figure 6, an internal standard curve for potassium. The internal standard curve for sodium was measured independently in three laboratories with three different sets of standards. In the figure, the group of points from each laboratory has been adjusted to correct for differences in the sensitivity that was used in each laboratory. Each point in this curve is the average of three or five measurements. Each point on the other curves represents a single measurement.

Interference. The filters should meet two requirements, high transmittance at the desired wave length and low transmittance at other wave lengths. In general, these are mutually dependent, so that a compromise must be made to obtain reasonably high sensitivity without excessive interference from the transmittance of unwanted light. The amount of interference between the different elements depends on the spectral response curve of the photocells and the natural emissivities of the different elements as well as on the properties of the filters. The composite effect of these has been measured as the concentration of each desired element which gives the same deflection as a high concentration of each interfering element. For example, a solution containing 1000 p.p.m. of sodium gave a deflection of 0.5 division through the potassium filter; 10 p.p.m. of potassium through the same filter gave a deflection of 45, so that $^1/_9$ p.p.m. of potassium would have given a deflection of 0.5. The interference factor was 1 in 9000. The interference factors of all the filters are given in Table I.

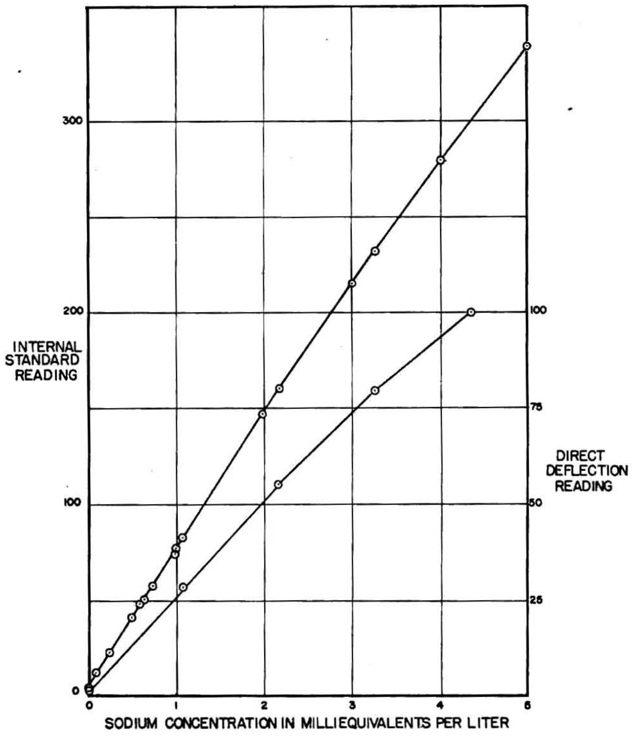

Figure 5. Direct and Internal Standard Calibration Curves for Sodium

The measurement of interference factors for the sodium filters was limited by the presence of sodium in the potassium, lithium, and calcium available for test solutions. In all cases the *D* lines were clearly visible in the flame with a spectroscope. When the emission from the concentrated calcium, lithium, or potassium solution was measured through sodium filter II, the insertion of Corning filter 2412, which removed the sodium light but transmitted the calcium, lithium, and potassium light, reduced the deflection by more than 80%. The principal parts of the deflections measured for the lithium and potassium solutions through sodium filter I were also due to the sodium impurity. These interference factors for the sodium filters would probably have been several times larger if measured with pure materials. For calcium interference, the impurity was not significant with sodium filter I.

Calcium filter I is suitable for the determination of relatively large amounts of calcium, but a correction must be applied if lithium or much potassium or sodium is present. In serum analysis

Table II. Approximate Calculation of Errors Due to Interference Factors

Sample contained 10 p.p.m. of sodium, 1000 p.p.m. of calcium, and 10,000 p.p.m. of potassium, with 500 p.p.m. of lithium added as internal standard.

Component	Apparent Concentration of Sodium and Lithium Due to Different Components, P.P.M.			
	Na filter I	Li filter I	Na filter II	Li filter II
10 p.p.m. Na +500 Li	10	500	10	500
1000 p.p.m. Ca	10	2.5	1.7	1
10,000 p.p.m. K	1	250	1	5
Total	21	752.5	12.7	506

Concentration by internal standard

$$21 \times \frac{500}{752.5} = 14.0 \text{ p.p.m. for filter I combination}$$

Concentration by internal standard

$$12.7 \times \frac{500}{506} = 12.6 \text{ p.p.m. for filter II combination}$$

these corrections require that the standards be made up with concentrations of sodium and potassium proportional to those of normal serum. Calcium filter II has more favorable interference factors and is useful for measurements with lithium as an internal standard.

The significance of the interferences is shown by an example of a low-sodium food sample containing 10 p.p.m. of sodium, 1000 p.p.m. of calcium, and 10,000 p.p.m. of potassium. When 500 p.p.m. of lithium have been added as an internal standard, the errors calculated approximately in Table II should result. An interference factor of 1 in 10,000 instead of 3000 is assumed for potassium through the sodium filters, as this makes a reasonable allowance for the contamination of the potassium sample mentioned above.

By direct intensity measurements the calculated errors are 110 and 27% for the I and II pairs of filters, respectively. By internal standard, these are reduced to 39 and 26%. The improvement with the I filters by internal standard is fortuitous, as it is caused by cancellation of two errors arising from different interfering elements. In the analysis of samples like this, filter combinations I might be expected to give errors up to about 100%, filter combinations II up to about 30%. Both of these could be reduced by adding comparable amounts of the interfering elements to the standards or by correcting for known interferences.

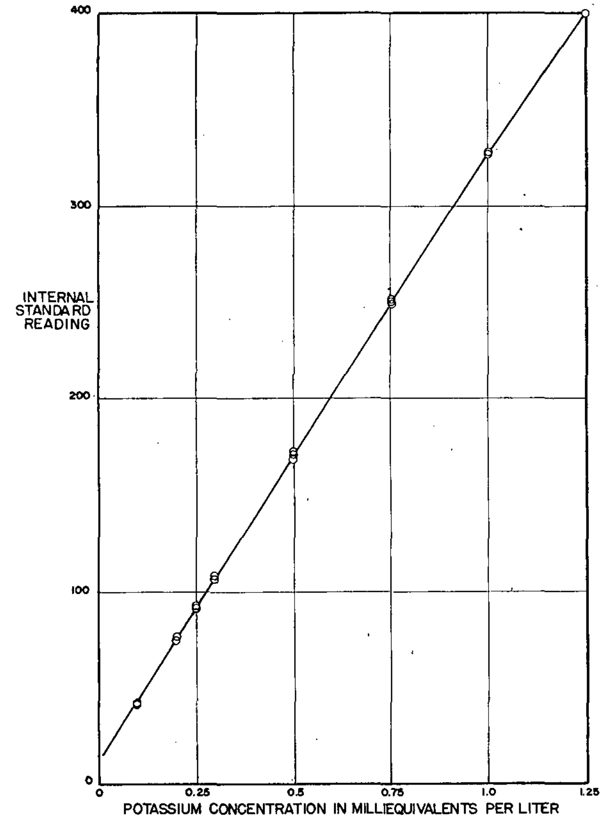

Figure 6. Internal Standard Calibration Curve for Potassium

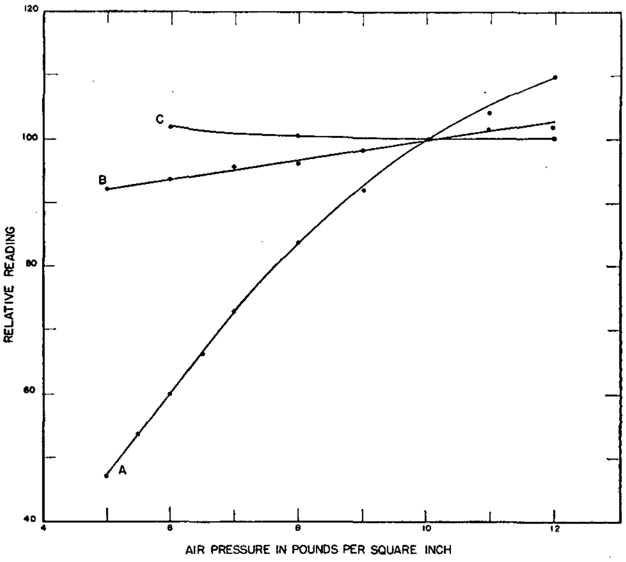

Figure 7. Effect of Change in Air Pressure

A. Direct intensity
B. Internal standard, 144 me. per liter (1000 p.p.m.) of lithium
C. Internal standard, 72 me. per liter (500 p.p.m.) of lithium

In this calculation nonlinearity at the high potassium concentration would reduce its interference from that above. This calculation considers only optical interference due to incomplete spectral isolation. There may be other interatomic effects in the flame that contribute equal or larger errors.

Stability. To test the stability and reproducibility, sodium was selected as the element to be measured, since many analyses call for the greatest accuracy in its determination. Its concentration in the samples used for tests was kept in or near the range below 2.5 me. per liter (59 p.p.m.), where the intensity of the *D* lines emitted was linearly proportional to the sodium content of the sample. For direct intensities, 1.09 and 2.18 me. per liter (25 and 50 p.p.m.) were used, and for the internal standard ones the same with 72 and 144 me. per liter (500 and 1000 p.p.m.) of lithium added. In some cases a wetting agent was also added, though it did not prove to have any effect on the readings.

The effect of changing the air pressure on the direct intensity reading was measured under different conditions to test its independence of the burner adjustments. When all other variables were held constant, the rate of change of intensity with air pressure was the same for three different gas pressures, for four different air inlet settings, and for three different sizes of gas jet. The range of the variables covered the range through which the burner operated well. Changing the air pressure appeared to affect only the amount of sample going into the flame without interrelated effects between it and the size or kind of flame.

A number of factors besides pressure affect the atomizer's performance. The principal ones are the size and orientation of the atomizer jets, the size and shape of the atomizer chamber, the position of the atomizer in it, and the pressure drop in the lines leading to and from the atomizer and chamber. Changing them changes the deflection but does not have much effect on its rate of change with air pressure.

Figure 7 shows in curve *A* the effect of air pressure change on direct intensity. A given percentage change in air pressure produces half as great a percentage change in direct intensity reading at high pressures, with larger changes at low pressures, as found by Berry. The internal standard readings using 144 me. per liter (1000 p.p.m.) of lithium shown in curve *B* are only about a fourth as much affected as the direct ones. With 72 me. per liter (500 p.p.m.) of lithium, curve *C* shows that the dependence on air pressure is reduced almost to zero, as found by Fox. The reading passes through a minimum around 10 pounds. The difference between these and the reduction by 2.5 found by Berry with 144 me. per liter of lithium may well be due to the faster flow of his atomizer, which made the concentration of both the lithium and sodium atoms in his flame higher. At the concentrations used, there is practically no reabsorption of sodium light in the flame, but there is enough reabsorption of lithium light to make a proportional increase in the concentration of both elements appear as a relative increase in the amount of sodium.

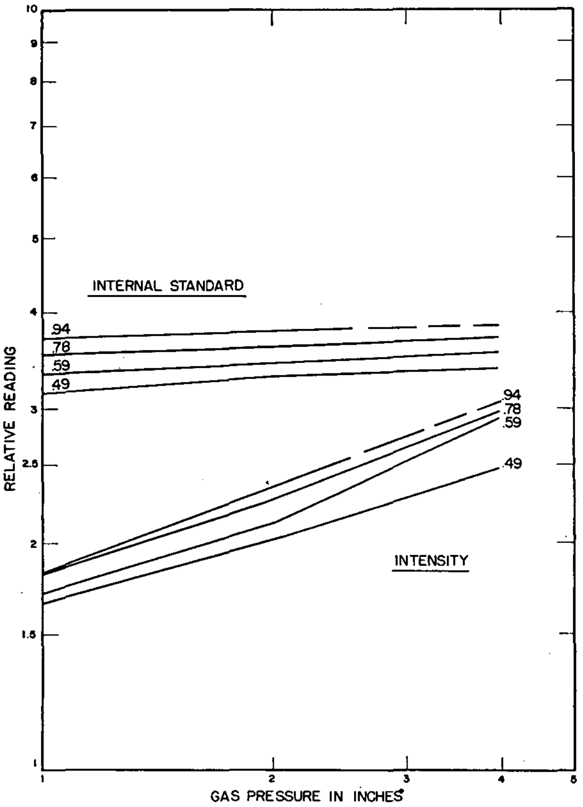

Figure 8. Effect of Changing Gas Pressure

0.100-inch gas jet and different air inlet openings

The effect of changing gas pressure was measured at constant air pressure for different air inlet settings and for different gas jet sizes. Figures 8, 9, and 10 show how the direct intensity and internal standard readings varied with gas pressure. In each figure air inlet areas are expressed in square inches. The curves for the 0.052-inch jet are not given, as they were too erratic to be useful. The data show that the minimum intensity was about the same for each jet at the smallest gas pressure and air inlet setting at which the burner would operate. The intensity increased with gas pressure and with the amount of primary air. The rate of increase was greatest for the smallest jet and smallest for the largest one. The percentage change in the readings for a given percentage change in gas pressure is proportional to the slope of the curves, which varies from 0.3 to 0.9 for different jet sizes and air inlet settings. The least slopes are about the same for each jet and occur with the minimum amount of primary air. They always increase as the air inlets are opened, but do so more rapidly for small jets than for large ones.

The internal standard curves are considerably less steep than those of the direct intensities. The improvement in stabilization varies from a factor of 10 in the most favorable conditions to 5 in the less favorable but usable ones.

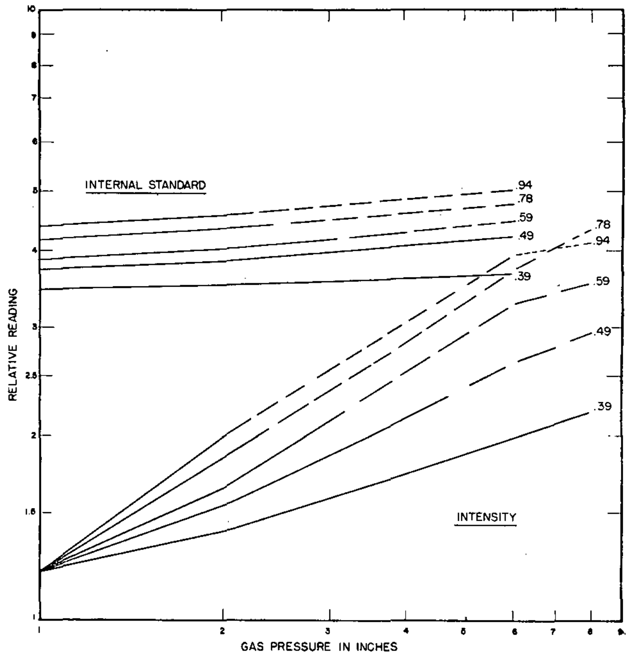

Figure 9. Effect of Changing Gas Pressure

0.082-inch gas jet and different air inlet openings

Reproducibility. The reproducibility of the flame as a source of radiation was measured by making a series of approximately 30 readings in 7.5 minutes and calculating for each series the average departure from the mean. These average differences are called the average noise level when expressed as percentages of the mean readings.

The noise level was found to be independent of air pressure over a wide range, so long as the air flow was below a critical rate. Above this rate, drops were picked up from the walls of the atomizer chamber and blown into the atomizing jet and into the base of the burner. From 6 to 12 pounds' air pressure, the noise level averaged 1.2% by direct intensities; at 14 pounds, it was 4.3%. Using 144 me. per liter (1000 p.p.m.) of lithium as an internal standard, the noise level was 0.5%. It decreased as the air pressure was reduced. When the lithium concentration in the sample was reduced to 72 me. per liter (500 p.p.m.) values of 0.3 to 0.4% were obtained.

Other series of measurements showed that the noise level was the same with sodium concentrations of 25 and 50 p.p.m., both by the direct and by the internal standard methods; the blue light emitted by the flame in the absence of sample was about twice as steady as the sodium series under the same conditions; and the stabilities of direct measurements of lithium and potassium were essentially the same as those of sodium.

The fact that both the observed noise level and the rate of change of internal standard reading with air pressure went down when the lithium concentration was reduced suggests that the residual noise level was associated with the air supply and atomizer. It may have been affected by variations in atomizer performance, caused either by small changes in air pressure or by turbulence and other conditions around the atomizer.

The noise level was also measured as a function of gas pressure and burner adjustments, using both the direct and internal standard methods. When the conditions were well stabilized, the noise was about the same for all direct intensity readings, with perhaps slightly better performance at the smallest usable air inlet openings. The fluctuations in the internal standard readings also were almost independent of conditions but slightly less than half as large as those for direct intensity. The range of measurements included gas jet diameters of 0.070 and 0.100 inch, gas pressures from 1 to 6 inches, and air inlet openings from 0.29 to 0.94 square inch.

Several series of internal standard measurements were made in which the sensitivity of the instrument was adjusted by standardizing on a reference solution before each reading. All were made with 9 pounds' air pressure, 4 inches' gas pressure, gas jet diameter 0.070 inch, and air inlet opening 0.15 square inch. Some series used 144 me. per liter (1000 p.p.m.) of lithium and sodium concentrations of 2.18 and 3.27 me. per liter (50 and 75 p.p.m.); others, 72 me. per liter (500 p.p.m.) of lithium and sodium concentrations of 1.09 and 1.74 me. per liter (25 and 40 p.p.m.). Neither showed the slow variations of the other series, their readings appearing to have only random fluctuations. The average difference from the mean was only ±0.3% for each. As this short-time reproducibility is representative of the operating procedure actually used in analyzing an unknown sample, this is the amount of fluctuation that might be achieved under well-stabilized conditions.

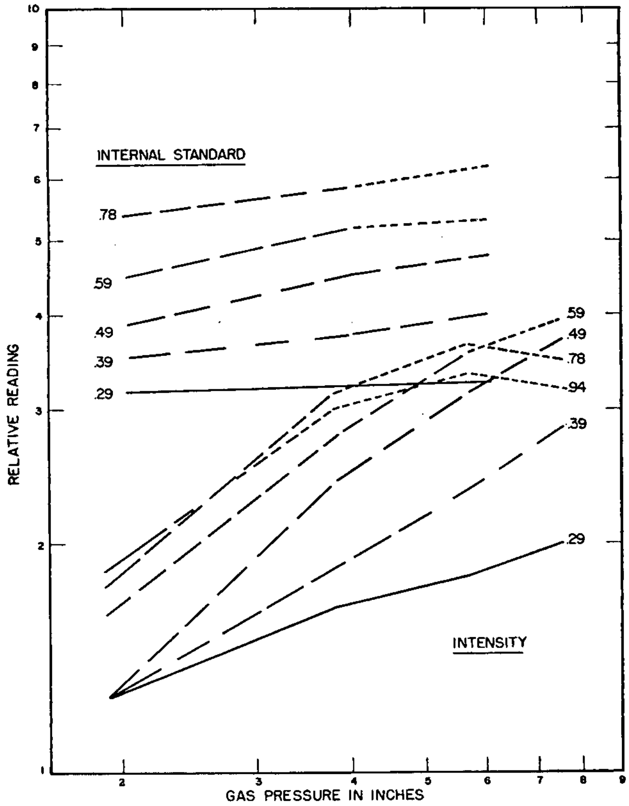

Figure 10. Effect of Changing Gas Pressure

0.070-inch gas jet and different air inlet openings

If the gas and air pressures vary, their effects are additional to this. The percentage change in either of them that would contribute an equal amount of variation with favorable instrument settings is ±10% for gas pressure, ±2% for air pressure with 144 me. per liter of lithium, and considerably more for air pressure with 72 me. per liter of lithium. These are variations that might be expected to occur under normal conditions where the gas supply is not regulated and a single regulator is used on the air supply. When the variations are larger than these, they contribute the principal part of the noise. The mean noise level was measured under such conditions and found to be ±0.5%. This may be expected to vary from time to time depending on the loads on the supply lines.

DISCUSSION

The results above indicate the most favorable operating conditions for the flame photometer burning this gas. The best air pressure is the highest that does not cause an increase in the noise level. The best gas jet and air inlet openings can be picked out of the figures as those that give the highest intensity and least slope at the available gas pressure. However, if the heat content of the gas is different, compensating adjustments must be made to keep the same actual conditions in the flame.

It has been the author's experience that the appearance of the flame is a reliable guide to its proper adjustment. In general, increasing the size of the gas jet with constant gas pressure increases the size of the flame and the intensity of the light emitted. If the gas pressure is low, the jet should be large; if it is very high, it may be advantageous to reduce it by putting a fixed constriction in the line so that a larger jet may be used. The air inlets control the amount of primary air in the flame. At very small openings, the flame lifts off the top of the burner. At larger ones it burns directly over the grid in little green cones. Next, the cones turn blue. Finally, at very large openings the cones lose their tops and give the flame a fuzzy appearance. With the largest jet, the flame did not get enough air to turn blue even with the air inlets wide open. If the gas has a higher heat content, more air is needed to burn it, and a smaller gas jet must be used to get equivalent flame conditions.

The color and appearance of the flame are indicated in Figures 8, 9, and 10. The solid lines indicate that the flame had green cones, the dashed ones that it had blue cones, and the dotted ones that it appeared fuzzy.

To get high sensitivity, high intensity is needed. This is best combined with relatively noncritical conditions at large jets and moderate gas pressure giving the largest flames that do not cause overheating. The conditions of a small jet and high gas pressure, where the curves might appear to indicate invariance, are not favorable, as the readings are very dependent on air inlet opening and tend to vary erratically.

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Interlaboratory Study on Determination of Acetyl in Cellulose Acetate

Progress Report by Subcommittee on Acyl Analysis, Division of Cellulose Chemistry Committee on Standards and Methods of Testing

The Eberstadt method, as now used for the determination of acetyl in cellulose acetate, was investigated by an interlaboratory study. Two samples of commercial cellulose acetate were analyzed by nine laboratories, and in each laboratory two analysts analyzed each sample in duplicate on three different days. The results, which are a measure of the performance of this method in practical use, show that the agreement between duplicates is good, the precision of the various operators and within the various laboratories is generally satisfactory, but the agreement between laboratories leaves much to be desired. The accuracy is, therefore, not good in some cases. Precision was evaluated by means of an analysis of variance. Three times standard deviation limits varied from ±0.12% acetyl for laboratory averages to ±0.8% acetyl for single values run by any operator in any laboratory. The accuracy was also investigated by determining hydroxyl contents and calculating acetyl by difference. This indicated that the average of all values was close to the probable true value for each sample. The causes for the variations observed were not completely established. Deviations from the procedure and insufficient time of contact of standard acid with regenerated cellulose during the back-titration accounted for some of the larger variations. This method is offered as a tentative standard for the determination of acetyl in cellulose acetate. Criticisms and suggestions for its improvement will be welcomed by the subcommittee. The subcommittee has gained in experience with interlaboratory testing of methods.

THE Subcommittee on Acyl Analysis of the Division of Cellulose Chemistry was organized in 1940 with Kyle Ward, Jr., as chairman. (It has also been called the Subcommittee on Acetyl and Formyl Analysis.) Methods of analysis were reviewed and a preliminary interlaboratory study was conducted in which samples of ground wood, wood pulp, cellulose acetate, and glucose pentaacetate were analyzed for their acetyl contents by the Eberstadt method and by a distillation method, and for their formyl contents by the mercuric chloride method. This study showed:

Each method is limited in its applicability.
Little formic acid was encountered in these samples.
Considerable and unexplained variations were found among laboratories.
The Eberstadt method was judged to merit further study.
Samples and methods submitted for future study should first be thoroughly tested in one laboratory.

The present study was undertaken with the following objectives:

To study the Eberstadt procedure for the determination of acetyl in cellulose acetate by a systematic plan.
To evaluate precision.
To evaluate accuracy.
To gain experience with interlaboratory testing of analytical methods.

The Eberstadt method (*3*, *4*, *6*), which has been adopted by the American Society for Testing Materials (*1*), is particularly applicable to commercial acetone-soluble cellulose acetates. Cellulose acetates of higher acetyl content (42 to 44.8%) usually require a longer saponification time (3 days instead of 2). Samples having less than 36% acetyl can also be analyzed by this method.

PROCEDURE

A systematic plan of investigation was set up involving the analysis of two samples in nine different laboratories, each laboratory having two analysts analyze each of the samples in duplicate on three different days. Apparatus was to be checked, solutions to be standardized, preferably using potassium hydrogen phthalate and phenolphthalein for the alkali standardization, and a practice run was to be made, particularly if the analyst was inexperienced with this procedure.

The samples submitted were: (1) a Wiley-milled commercial cellulose acetate of about 40.5% acetyl, and (2) a powder-precipitated commercial cellulose acetate of about 39% acetyl. These were thoroughly analyzed by one laboratory and were known to be homogeneous and stable.

The instructions for the analyses were as follows (certain desirable changes or additions brought out by this investigation are given in parentheses).

Reagents.
1. 75% by volume ethyl alcohol; alcohol denatured by the 3A formula is satisfactory for this purpose.
2. Standard 0.5 *N* sodium hydroxide.
3. Standard 0.5 *N* hydrochloric acid.

Procedure. Grind the sample in a Wiley mill or other suitable grinder so that 100% will pass a No. 20 (840-micron) sieve. Dry the sample at 100° to 110° C. for 2 hours and cool in a desiccator. (An oven with mechanical circulation is to be preferred over a convection-type oven.) Accurately weigh duplicate 1-gram samples and place in 250-ml. Erlenmeyer flasks.

This procedure requires accurately weighed dry samples. Accurate weighing is readily accomplished at relative humidities below 75%, but above this value the moisture regain is so rapid that the following variation in the procedure should be used:

Dry approximately a 1-gram sample in a weighing bottle, stopper, and cool in a desiccator. Weigh the bottle containing the sample, transfer the sample to a flask, and weigh the bottle again to obtain the sample weight. Handle the bottle either with tongs or a clean, dry cloth during these manipulations.

Add 40 ml. of 75% alcohol to each sample. Include at least two blanks with each set of samples (and carry the blanks through the complete procedure, including the back-titration). Heat the flasks loosely stoppered for 30 minutes at 50° to 60° C. Add 40 ml. of a standard 0.5 *N* sodium hydroxide to each flask and heat again at 50° C. for 15 minutes. Stopper the flasks tightly and allow to stand at room temperature for about 48 hours.

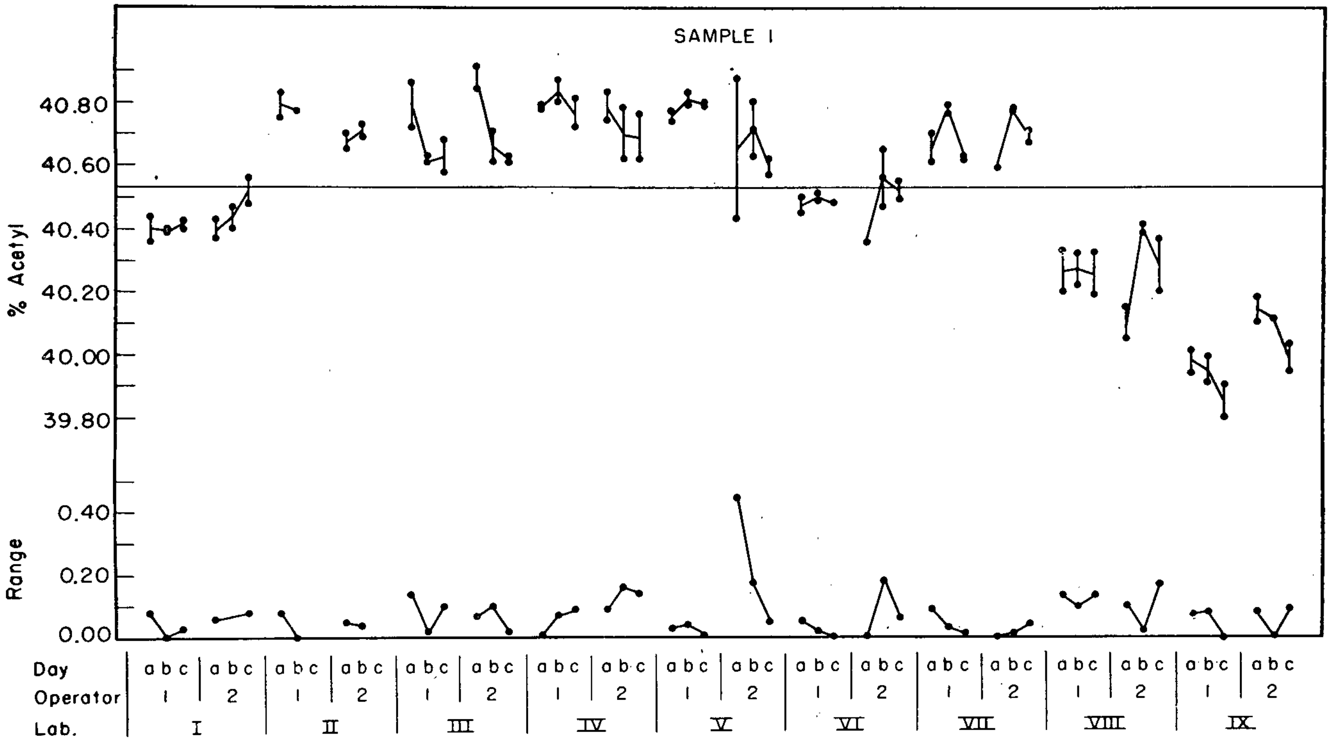

Figure 1. Data Reported on Sample 1

At the end of this time back-titrate the excess alkali with standard 0.5 N hydrochloric acid, using phenolphthalein indicator. Add an excess of about 1 ml. of acid and allow the alkali to diffuse from the regenerated cellulose for several hours or (preferably) overnight. The disappearance of the pink color indicates the complete neutralization of the alkali. Titrate the small excess of acid with alkali to a phenolphthalein end point.

Table I. Analysis of Variance

Source of Variation	F Ratio	
	Sample 1	Sample 2
Laboratories	45[a]	42[a]
Days	2.3[b]	3.0[b]
Operators	1.5	1.3
Duplicates	...	....

[a] Significant at 0.5% probability level (F = 7.7).
[b] Significant at 1.0% probability level (F = 2.2).

Extreme care must be taken to locate this end point. After the sample is titrated to a faint pink end point, stopper the flask and shake vigorously. The end point may fade because of acid diffusing from the cellulose. Continue the addition of alkali and shaking until the faint pink end point remains after vigorous shaking of the flask.

Calculation

$$\% \text{ acetyl} = \frac{\left[\frac{\text{blank}}{(\text{ml. of HCl} \times N - \text{ml. of NaOH} \times N)} - \frac{\text{sample}}{(\text{ml. of HCl} \times N - \text{ml. of NaOH} \times N)}\right] \times 4.3}{\text{sample weight}}$$

Report results to four significant figures.

The data were reported on sheets coded to conceal the identity of the laboratory and the analysts. The primary standard used, the drying procedure, dates on which analyses were run, and a statement as to whether or not the operators had had previous experience with this procedure were also recorded.

Table II. Precision

Lab.	Operator	Days	Values	3-Sigma Control Limits, % Acetyl	
				Sample 1	Sample 2
Laboratory Average (12 Determinations)				±0.12	±0.11
1	1	1	Av. of dupl.	±0.15	±0.15
1	1	Any	Av. of dupl.	±0.23 (0.24)[a]	±0.24 (0.30)[a]
1	Any	Any	Av. of dupl.	±0.25	±0.25
1	Any	Any	Single	±0.29 (0.35)[a]	±0.28
Any	Any	Any	Single	±0.85	±0.78

[a] Long-time experience of one laboratory.

DATA

Figures 1 and 2 present the data obtained on the two samples. Examination of these data leads to the following observations:

The agreement of duplicates is good in most cases.

Fairly good reproducibility of results was obtained by each analyst and each laboratory.

There was considerable variability among laboratories, and, in general, this was consistent for both samples.

Thus, fairly good precision was obtained, but the accuracy in many cases was not all that is to be desired.

EVALUATION OF PRECISION

The data obtained were subjected to an analysis of variance by the procedure described by Brownlee (*2*) and yielded the results shown in Table I. These indicate that the variations among operators are small. The variations on different days are only slightly greater than the variations among operators, and the variations among laboratories are great.

The components of variance were then determined and the statements of precision shown in Table II were calculated from these data. The limits in parentheses were found experimentally

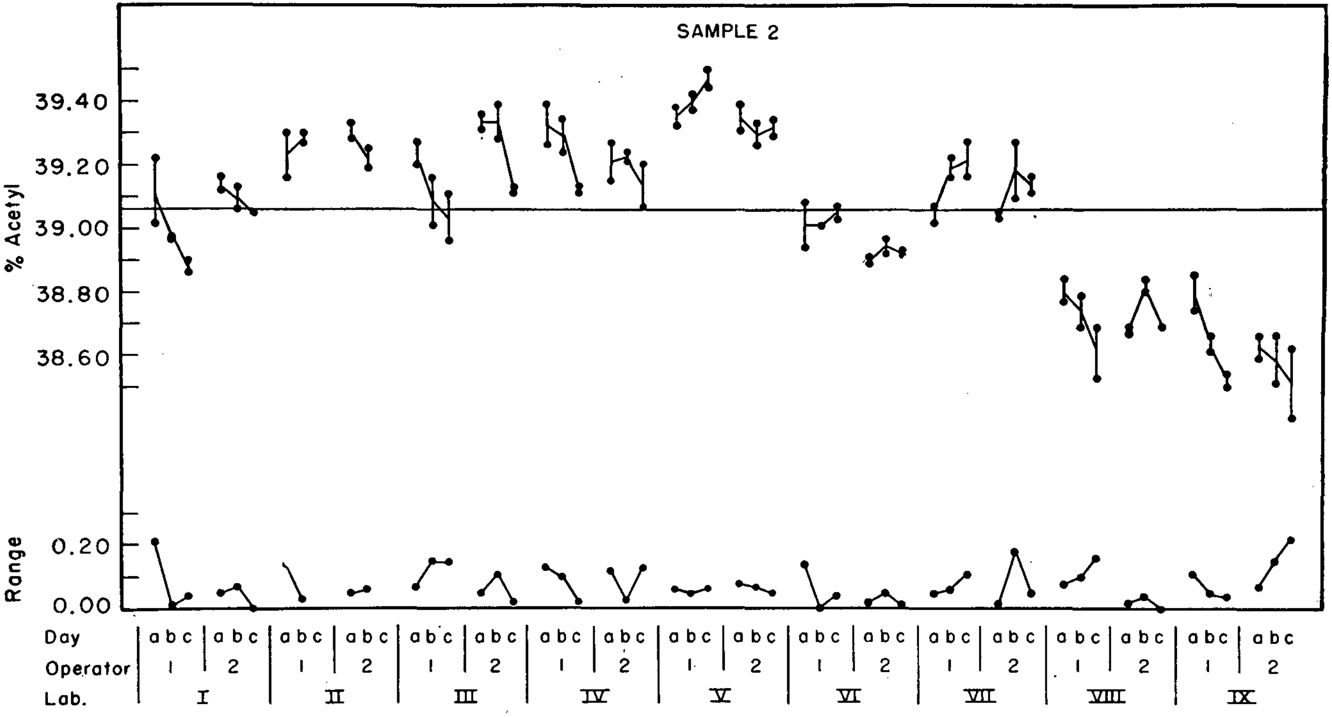

Figure 2. Data Reported on Sample 2

in one laboratory and are included for comparison. The results are expressed in 3-sigma (three times standard deviation) units; values outside these limits can be considered to be out of control

ACCURACY

Results of the analysis of samples 1 and 2 are summarized in Table III. (All the data in this table except the test averages were determined in one of the collaborating laboratories.) These data indicate that the true analysis of sample 1 is very close to 40.5% and for sample 2 is about 39.0% acetyl. The results from this investigation average slightly high, and the long-time results obtained by one laboratory tend to be slightly low. The low results can be explained at least partially for sample 1 by the fact that precautions to avoid moisture regain during weighing of the sample were not taken at all times during the 4 years through which these data were collected. The hydroxyl results were obtained in the first case by the acetylation procedure described by Malm, Genung, and Williams (*5*) and were confirmed by a new procedure developed by Tanghe (*7*). Hydroxyl values were calculated to the corresponding acetyl values by:

$$\% \text{ acetyl} = 44.8 - 1.42 \times \% \text{ OH}$$

Figure 3 shows the laboratory averages and control limits based on variations of operators and days, but excluding interlaboratory variations. These are the limits to be sought, but they have not yet been attained.

SOURCES OF ERROR

The probable sources of error are listed in Table IV. In an interlaboratory study of this sort, variations listed under "General" may occur, but they probably account for only part of the variations observed. High results would be expected if the saponifications were conducted at a temperature above about 35° C. High results due to end-point error (the most probable one) occur if an insufficient time is allowed for the small excess of acid to penetrate the cellulose fibers and neutralize all the alkali during the back-titration. The amount of time required for this diffusion might be expected to vary from sample to sample, depending on the physical condition of the regenerated cellulose, and is from several hours to overnight.

Laboratories 3, 4, 5, and 9 have reported data from reanalysis of these samples, and their results are compared in Table V. Laboratory 3 found that extending the diffusion time from 5 hours to 24 hours made the difference between high values and acceptably accurate results. Laboratory 4 had used 1 *N* acid for back-titrations. Reanalysis using the specified 0.5 *N* acid and follow-

Table III. Accuracy

	Sample 1	Sample 2
Acetyl, %		
Av., this test	40.53	39.05
Av., one laboratory		
1. Av. of 213 values over 4 years	40.42 ± 0.35[a]	..
2. Av. of over 20 values	..	38.97
Calcd. from hydroxyl analyses		
Acetylation method		
1. 3.022 ± 0.41[a]% OH (av. of 112 values)	40.51 ± 0.5[a]	..
2. 4.08% OH	..	39.0
New procedure		
1. 3.025% OH (av.)	40.50	..
2. 4.10% OH(av.)	..	38.97
Ash, %	0.08	0.02
Sulfur, %	0.015	0.009
Carboxyl, %	0.04	0.03

[a] 3-sigma limits for these data.

Table IV. Sources of Errors

General	High Results	Low Results
Standard solutions	Temperature	Incomplete drying
Weights	End-point error (alkali left in cellulose)	Moisture regain during weighing
Volumetric glassware		
Deviations from procedure		End-point error (acid left in cellulose)

ing the procedure strictly produced good results. Laboratory 5, with no change in procedure, first confirmed its earlier results. When the diffusion time was extended, more precise and somewhat lower results were found. Laboratory 2 reported that a 5- to 6-hour diffusion time was used for its analyses. The results are similar to those from Laboratories 3 and 5 when less than 24-hour diffusion times were used. Laboratory 9, which had obtained the lowest results, reported higher values and explained the difference as being mostly due to the treatment of the reagent blank, which was not exactly according to instructions in the first test.

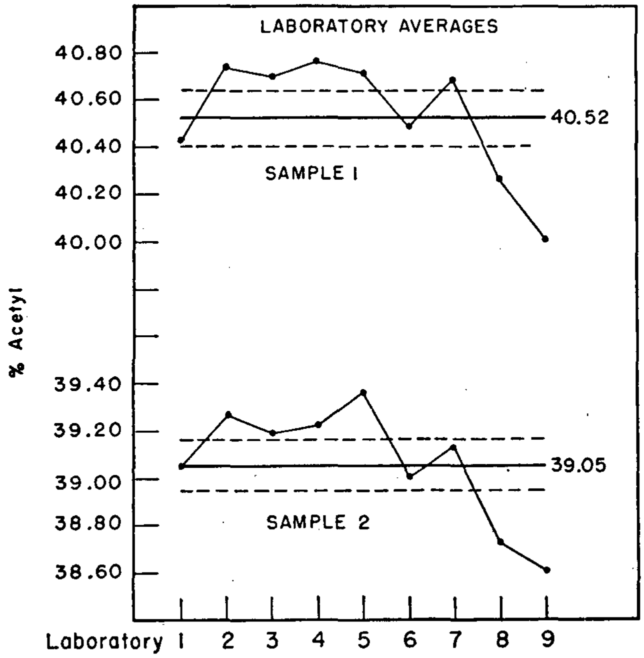

Figure 3. Comparison of Laboratory Averages with Control Limits Based on Variations Due to Operators and Days Only

Table V. Results of Reanalysis

	Sample 1	Sample 2
Lab. 3		
Test average	40.70	39.19
Reanalysis		
5-hour diffusion	40.91, 40.71	39.27, 39.30, 39.31
24-hour diffusion	40.46, 40.57	39.00, 39.10
Lab. 4		
Test average	40.76	39.22
Reanalysis	40.46,40.46	39.13, 39.14
Lab. 5		
Test average	40.72	39.36
Reanalysis		
Usual procedure	40.67, 40.83, 40.69	39.43, 39.23, 39.45
2-hour diffusion	40.48, 40.64, 40.21	39.37, 39.50, 39.24
24-hour diffusion	40.57, 40.59, 40.62	39.17, 38.91, 39.13
Lab. 9		
Test average	40.00	38.61
Reanalysis		
(av. of 24)	40.42	38.88

The time and care required in locating the exact end point are shown to be important. Good results can be obtained if sufficient time is allowed for diffusion of the reagents. Suggestions have been made that this time can be shortened by shaking or tumbling the sample or by adding a larger excess, such as 10 ml., of acid in the first back-titration. These suggestions have not yet been tested by the subcommittee.

TEST EXPERIENCE

The subcommittee has gained experience with interlaboratory tests and offers the following comments:

Thorough investigation of the method and samples by one laboratory and a good plan can save time and effort for the group of laboratories.

Modern statistical techniques are useful for presenting data and for evaluating precision.

Strict adherence to the procedure and complete cooperation are vital. Data should be complete for each laboratory to be usable in the statistical calculations.

Standard solutions or control samples should be included to evaluate some of the variables or parts of the procedure. For example, if a sample of standard acid had been included in this study, variations due to alkali standardization could have been evaluated.

TENTATIVE STANDARD METHOD

This procedure is considered to be generally applicable and desirable as a referee method for analysis of cellulose acetates. It is offered as a tentative standard method. Criticisms and suggestions for its further improvement will be welcomed by the subcommittee.

COLLABORATORS

These investigations have involved collaboration of many people in several different organizations. The organizations and their representatives on the subcommittee are as follows:

American Viscose Corp.	L. A. Cox
Celanese Corp. of America	E. S. McColley
Eastman Kodak Co.	L. B. Genung, Chairman
E. I. du Pont de Nemours & Co., Inc.	Eugene Johnson
Hercules Powder Co.	L. R. Kangas H. G. Tennant[1] J. Barsha[1]
Institute of Paper Chemistry	B. L. Browning M. A. Heath[1] D. R. Moltzau[1]
Southern Regional Laboratory	Kyle Ward, Jr., Past Chairman C. L. Hoffpauir R. E. Reeves[1]
Tennessee Eastman Co.	D. E. Northrop
Weyerhaeuser Timber Co.	R. N. Hammond

[1] Past members.

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Determination of Microgram Quantities of Sulfide Sulfur

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A reliable method is needed for the determination of microgram quantities of hydrogen sulfide and sulfur in metal sulfides. A volumetric method based on the oxidation of hydrogen sulfide into sulfate by means of alkali hypochlorite has been investigated. Systematic studies show that this reaction is influenced by the pH and the temperature of the hypochlorite solution. Quantitative oxidation of sulfide into sulfate occurs, at room temperature, in hypochlorite solutions of pH between 8 and 11 and between 14 and 15. In the intermediate pH range the oxidation is incomplete, and colloidal sulfur is formed. The lowest yield, at 0° C. and pH 12, corresponds to about 50% oxidation to sulfate. As most favorable for analytical work a hypochlorite solution of pH 14.4 is suggested. The method can be used for determining sulfur whenever it is present as hydrogen sulfide, or can be converted into it.

FOR the determination of small amounts of hydrogen sulfide, or sulfide sulfur that can be converted into hydrogen sulfide by acid evolution, various methods may be used. Probably the most common is based on the oxidation of hydrogen sulfide with iodine to form elementary sulfur, either by titration with a standard iodine solution (*3*) or by addition of excess iodine and back-titration with thiosulfate. As this reaction utilizes the exchange of 2 electrons only per atom of sulfur, the amount of iodine consumed is relatively small, and very dilute iodine and thiosulfate solutions are needed when microgram quantities of sulfur are to be determined.

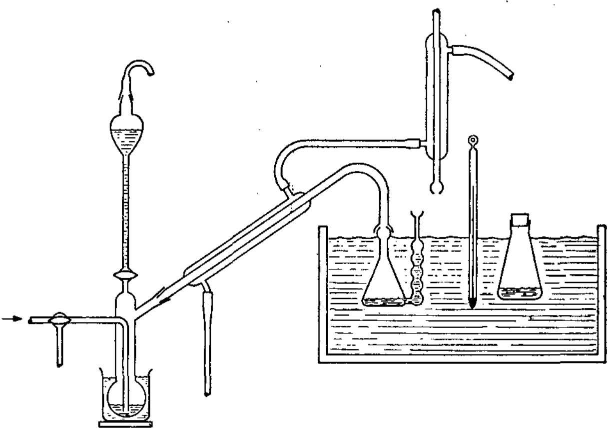

Figure 1. Apparatus for Evolution and Absorption of Hydrogen Sulfide

A better method would be one where the hydrogen sulfide is oxidized to sulfate, corresponding to the exchange of 8 electrons per atom of sulfur. The most suitable oxidizing agent in this respect seems to be hypochlorite solution. This type of analysis has been mentioned (*1*, *2*), but without description of the exact procedure to be followed. Recently Pepkowitz (*5*) presented an account of his study on microdetermination of sulfur by oxidation to sulfate with calcium hypochlorite solution. Pepkowitz did not obtain a theoretical yield of oxidation, but suggested the use of an empirical factor which can be obtained by standardization with known amounts of alkali sulfide.

Attempts were made in the authors' laboratory to employ this method for the analysis of hydrogen sulfide and iron sulfide using solutions of commercial calcium hypochlorite (bleaching powder). The oxidation was, in many cases, closer to 50 than to 100%, and the empirical factor seemed to vary with the strength of the hypochlorite solution as well as with the temperature and the amount of sulfur in the sample. Therefore, to understand the reasons for this nonstoichiometric yield and to learn how this method could be best utilized, a systematic study of the effect of pH and temperature was made.

EXPERIMENTAL

Preliminary tests had shown that potassium hypochlorite behaved in the same manner as calcium hypochlorite and was equally stable with respect to time. As commercial bleaching powder was suspected to be of variable quality, the systematic work was based on the use of potassium hypochlorite solution.

In a small gas generator, similar to the one shown in Figure 1, about 3.2 grams of potassium permanganate were treated with 6 *M* hydrochloric acid and gently heated. The evolving chlorine was, by a flow of nitrogen, swept into 1 liter of 0.15 *M* potassium hydroxide solution, in which it was absorbed to give a solution of equal (0.5) molarity of potassium hydroxide, potassium hypochlorite, and potassium chloride. This served as a stock solution and it was stable when kept in a dark place at room temperature. After 2 months its strength had decreased about 4.5%.

For actual use the stock solution was diluted five times to give a solution which was 0.01 *M* with respect to potassium hypochlorite or 0.02 *N* as to oxidizing power. To obtain hypochlorite solutions of various pH values, dilute sulfuric acid or potassium hydroxide pellets were added.

The pH of the hypochlorite solutions to which acid had been added was measured potentiometrically with a Fisher Titrimeter using a Beckman glass electrode standardized against a buffer solution of pH 7. Without acid added, the solution showed by this method a pH of about 13. Its theoretical pH could be calculated from the composition (0.01 *M* potassium hydroxide, 0.01 *M* potassium hypochlorite, and 0.01 *M* potassium chloride) to correspond to 12.03. As the glass electrode used was recommended only for work at pH below 9, values at higher pH may be expected to be in error. Therefore, the pH of the original solution was taken as equal to the calculated value, 12.03, and the measured values were corrected downward by an amount which varied linearly from about one unit for the original solution to zero for pH 7.

For the solutions to which potassium hydroxide had been added, the pH was calculated assuming complete dissociation, and disregarding any change in activity coefficients as the concentration of potassium hydroxide increased. These values will, therefore, be rather formal, but give an approximate picture of the true pH. The small variation of pH with temperature was neglected throughout the entire composition range.

During the absorption and oxidation of hydrogen sulfide a small amount of sulfuric acid is formed which will change the pH of the solution somewhat. This effect can be calculated and is negligible for most of the pH range. It becomes significant only below pH 9.

A preparation of acid-soluble sulfide was made by mixing and grinding 1 part of iron sulfide of known sulfur content with about 350 parts of zinc dust (c.p., Eimer and Amend, New York, N. Y.). To obtain uniformity the mixture was agitated and rotated in a jar mixer for several weeks. The mixture thus obtained contained about 0.1% sulfur.

For each test an accurately weighed amount (0.63 to 0.64 gram) of this sulfide mixture was used, corresponding to 0.63 to 0.64 mg. of sulfur. In the apparatus shown in Figure 1 the mixture was treated with 6 *M* hydrochloric acid. During this operation the reaction flask was immersed in cold water, the temperature of which was gradually raised to boiling. When the sample had been completely dissolved, a vigorous stream of nitrogen was passed through the apparatus to assure complete transfer of hydrogen sulfide into the Volhard-type gas absorption flask. This contained 25 ml. of the 0.02 *N* hypochlorite solution to which acid or base had been added to give the proper pH. The absorption flask was immersed in a constant temperature bath and was, for runs at 60° C., equipped with a reflux condenser. A full hour was allowed for the solution of the sample and absorption of the gas. To reduce the possibilities for photochemical reactions, direct sunlight was avoided and some yellow dye was dissolved in the constant temperature bath.

Simultaneously, in a separate Erlenmeyer flask, a blank consisting of an equal amount of hypochlorite solution of equal basicity was kept in the constant temperature bath for the same length of time.

When the absorption was completed, 1 to 2 grams of potassium iodide were added to both solutions, and the solutions were acidified with acetic acid. About 5 ml. of 50% acetic acid were used, except for the more basic solutions where 7 ml. of 50% acid were used for each gram of potassium hydroxide added. The blank as well as the solution in the absorption flask was then titrated with 0.01 *N* thiosulfate solution using 1 ml. of 1% starch solution as indicator. The thiosulfate solution had been standardized against iodine, liberated with acid from a mixture of a weighed amount of potassium iodate and an excess of potassium iodide. The amount of hypochlorite consumed by the oxidation of hydrogen sulfide was then given by the difference between the titer for the blank and for the absorbing solution. The results were calculated as percentage of the theoretical oxidation of the hydrogen sulfide to sulfuric acid.

In Figure 2 are given the results obtained for four different temperatures and for pH values between 8 and 15. At 0° C. some runs were made in which the pH had been adjusted with hydrochloric acid instead of sulfuric acid. The two sets of values are in good agreement.

DISCUSSION

It follows from Figure 2 that approximately quantitative oxidation is obtained in the pH ranges from 8 to 11 and from 14 to 15. In the intermediate range the oxidation is incomplete. The oxidation is least complete at a pH of about 12—i.e., close to the pH of the hypochlorite solution with neither acid nor base added. The least oxidation occurs at the lowest temperature, 0° C., where the minimum corresponds very closely to 50% oxidation—i.e., an average exchange of 4 electrons per atom of sulfur. At higher temperatures the oxidation to sulfate is more complete, but certain deviations from a smooth curve appear at all temperatures in this intermediate pH range. For the deviations at 40° to 60° C. there are not enough data to say whether they correspond to reproducible maxima and minima, or are due to factors beyond control, such as traces of catalyzing impurities, photochemical reactions, or the rate of hydrogen sulfide introduction. In any case the spread of the points is definitely larger than the titration error. At 20° C. a narrow but reproducible peak appears at pH 12.

At pH around 8, the formation of undissociated hypochlorous acid becomes pronounced and some chlorine is swept out of the solution and is lost. This is the obvious reason for the apparent yield of oxidation higher than 100% at high temperature and low pH.

At very high pH, about 15, the yield of oxidation seems once more to decrease. This is probably connected with the formation of potassium chlorate. The titer for the blanks with pH below 14.5 remained practically constant during the run, whereas it decreased significantly at higher pH.

The products of oxidation in the intermediate range were determined qualitatively. It was apparent that colloidal sulfur was formed. In some cases, corresponding to the intermediate "maxima" at 40° to 60° C., sulfur could be observed during the initial part of the absorption, but it disappeared later on. In addition to colloidal sulfur, sulfate was formed. This was shown for some solutions of pH around 12: After absorption of hydrogen sulfide, the solution was treated with mercury or zinc dust and acidified with hydrochloric acid to remove hypochlorite and colloidal sulfur. After filtration, sulfate ion could be identified in the filtrate with barium chloride in the usual way. As other sulfur compounds are readily oxidized by hypochlorite, it seems that when the oxidation is incomplete, the end product is a mixture of sulfur and sulfate.

It is not the purpose here to try to explain the mechanism of this reaction or the reason for the incomplete oxidation. However, a few points should be mentioned:

1. A number of sulfur compounds are known with degree of oxidation between hydrogen sulfide and sulfuric acid, and it is likely that the oxidation goes through one or several of these compounds. From stereochemical considerations a possible intermediate compound would be sulfoxylic acid, H_2SO_2. The formation of this compound would correspond to the exchange of 4 electrons per atom of sulfur or 50% oxidation to sulfuric acid. As in no case less than 50% oxidation was observed, intermediate oxidation of hydrogen sulfide to elementary sulfur (corresponding to 25% oxidation to sulfuric acid) is regarded as less probable.

2. Several of these intermediate compounds are known either to disproportionate and give elementary sulfur or to react with each other to give sulfur.

$$2H_2SO_2 = H_2SO_3 + S^0 + H_2O$$

$$H_2SO_2 + H_2SO_3 = 2H^+ + SO_4^{--} + S^0 + H_2O$$

[According to the standard oxidation-reduction potentials listed by Latimer (*4*) these reactions may proceed as indicated, even in a basic solution. Whether they actually occur in the present case remains to be proved.]

3. Hydrogen sulfide, and several of the intermediate sulfur compounds as well as hypochlorous acid, are weak acids with at least one of their dissociation steps taking place in the pH range in question. It is therefore possible that in one pH range the

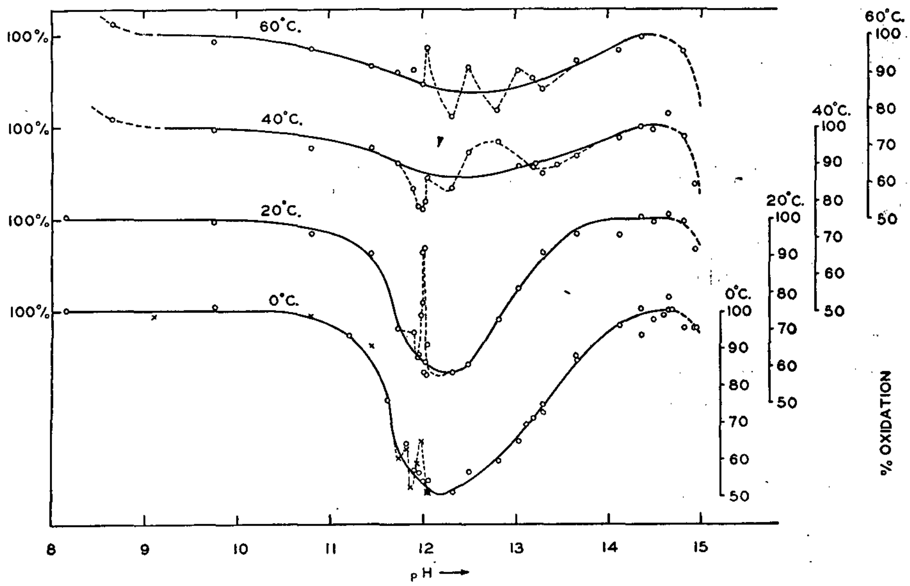

Figure 2. Percentage of Oxidation *vs.* pH of Hypochlorite Solution for Four Different Temperatures

Crosses represent solutions in which pH had been adjusted with hydrochloric acid (0° C. only). Dotted lines indicate possible details in curves

Table I. Results for Various Standard Samples

Material	Sample Weight	Sulfur Found	Sulfur Found	Accepted Value
	Grams	*Mg.*	*%*	*%*
NBS standard sample of steel 15d (0.054% Cu)	2.0561	0.650	0.0316	0.033–0.034
	2.0668	0.657	0.0318	
	3.4072	1.084	0.0318	
NBS standard sample of steel 8g (0.019% Cu)	2.1192	0.532	0.0251	0.025–0.026
	4.7387	1.180	0.0249	
New Jersey Zinc Co. ZnS[a]	0.00128	0.422	32.90	32.90
	0.00260	0.855	32.87	
	0.00401	1.321	32.95	
FeS + Zn, 1:350	0.7029	0.748	0.1063	0.106–0.107
	0.7622	0.806	0.1057	
	3.0091[b]	3.195	0.1062	

[a] Weighed on microbalance and mixed with 1 to 2 grams of zinc dust.
[b] 50 ml. of KOCl solution with 7 grams of KOH.

reaction is primarily between undissociated acids, in another between the ions, and in intermediate ranges partly between acids and partly between ions of various types. As stereochemical conditions probably are important for the choice of mechanism, the reaction path may be strongly affected by a slight change in pH.

4. Colloidal sulfur is more rapidly oxidized by hypochlorite in a strongly basic than in a neutral solution.

The over-all yield of oxidation as shown in Figure 2 may be a result of a combination of the various factors mentioned above. A tentative explanation for the incomplete oxidation would then be initial formation of sulfoxylic acid or its ion, which may react further according to the scheme outlined under point 2. The peak at 20° C. for pH 12 still represents an open question.

ANALYTICAL APPLICATIONS

The incomplete oxidation and poor reproducibility which were experienced when a solution of commercial bleaching powder was used as oxidizing agent may now readily be understood. Such a solution has a pH near 12.

For analytical work the ranges between pH 9 and 10 and between 14 and 15 seem to give the best possibilities. Attempts to work out a useful method in the lower basicity range were not very successful. It is difficult to adjust the pH of the solution to be just right. Some sulfuric acid is formed by the reaction and some hydrochloric acid may come over from the evolution flask and cause a large change in the pH. It might be possible to add an appropriate buffer to maintain correct basicity, but since the solution has to be acidified before titration, a buffer may require unreasonable amounts of acid for acidification.

The best results were obtained in the very basic range, and as standard basicity an addition of 3.5 grams (25 pellets) of potassium hydroxide per 25 ml. of solution was used. This corresponds to a 2.5 *N* potassium hydroxide solution, and a pH of about 14.4.

Various sulfides of known sulfur content and two Bureau of Standards steel samples were tested. The results of these analyses are listed in Table I.

It is apparent from the data given in Table I that under the right conditions this is a sensitive and accurate method. Its limitation for steel analysis lies in the fact that sulfur in steel may be present as sulfides, which are not soluble in acids. For example, steel 15d, for which slightly too low values were found, contained as much as 0.054% of copper. Steel 8g, on the other hand, contained only 0.019% copper and the analysis showed a perfect agreement with Bureau of Standards values.

SUMMARY

The oxidation of hydrogen sulfide with potassium hypochlorite was studied as a function of temperature and pH of the hypochlorite solution. Nearly quantitative oxidation to sulfate was obtained in the pH ranges from 8 to 11 and from 14 to 15. At intermediate pH values the oxidation was incomplete, and at 0° C. and pH around 12 the least oxidation was found, corresponding to the average exchange of 4 electrons per atom of sulfur. The products of oxidation were, in this range, a mixture of sulfate and colloidal sulfur.

The most favorable solution for the analysis of microgram quantities of hydrogen sulfide was found to be hypochlorite in a 2.5 *N* potassium hydroxide solution, corresponding to a pH of about 14.4.

ACKNOWLEDGMENT

The authors are indebted to N. H. Nachtrieb for valuable suggestions and criticism.

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Spectrographic Determination of Beryllium in Urine and Air

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THE recognition of beryllium as an extremely toxic metal when inhaled in minute quantities has stimulated analytical research directed at the accurate estimation of submicro amounts of this metal in air and urine. Various spectrographic procedures have been described in recent years (*1, 3, 4, 6*), all of which employ the direct current arc. A fluorometric method using morin, which achieves the desired sensitivity by using large quantities of urine, has also been described (*5*).

The present study was undertaken in an effort to develop a somewhat more rapid method, of acceptable accuracy and sufficient sensitivity to permit use of the relatively small samples of urine and air that might be collected routinely in beryllium-using industries. It was further desired to utilize an alternating current spark technique for solution analysis, on which research has been in progress for the past 2 years. This technique, which utilizes the Applied Research Laboratories rotating electrode assembly,

Beryllium has been demonstrated to be extremely toxic to man when inhaled in less than microgram amounts. This high order of toxicity has necessitated much more sensitive analytical methods than any previously in use, if tedious concentration procedures are to be avoided. In a rapid spectrographic method for determining hygienically significant amounts of beryllium in urine and air, suitably prepared solutions are analyzed directly by means of a rotating electrode using an alternating current spark; errors average about 10% of the amount present. Several direct current arc spectrographic procedures of the necessary sensitivity are cited, but no alternating current spark procedures have been published. The reduced number of manipulations afforded by the solution technique, with the inherent accuracy of the alternating current spark, ensures accuracy, speed, and ease of determination.

has been described for the determination of various metallic constituents in human plasma and urine (*2*, *7*).

REAGENTS

All reagents are analytical grade, except where otherwise indicated.

Nitric-Perchloric Acid Mixture. Add 3 volumes of nitric acid to 1 volume of 72% double-distilled perchloric acid.

Manganese Chloride Solution. Dissolve 1 gram of manganese chloride tetrahydrate in 100 ml. of distilled water.

Aluminum Internal Standard Solution. As described by Barnes (*1*), dissolve 0.750 gram of metallic aluminum in approximately 10 ml. of 1 to 1 hydrochloric acid and make up to 500 ml. with distilled water.

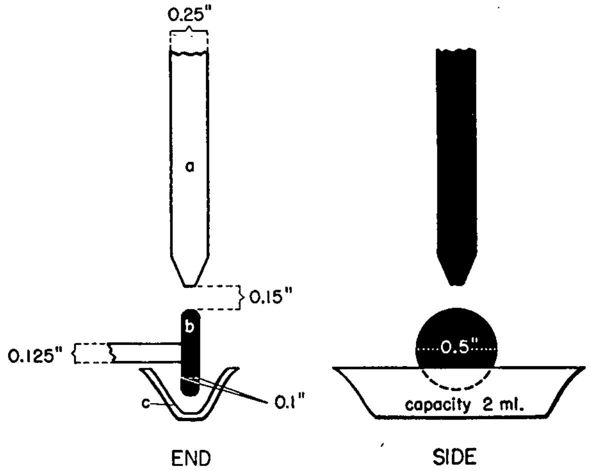

Figure 1. Assembly

Standard Beryllium Solution. As described by Barnes (*1*), dissolve a weighed amount of fused metallic beryllium in a small amount of 1 to 1 hydrochloric acid and dilute to volume with 1% hydrochloric acid, using a microburet and volumetric flasks. Standard solutions containing 0.01 and 0.001 microgram of beryllium per ml. have been used.

Ethylenediaminetetraacetic Acid Solution. The tetrasodium salt of this acid, available commercially as Versene liquid, 34% solution, Bersworth Chemical Co., has been found satisfactory. Analytical reagent grades of similar compounds are available.

SPECTROGRAPHIC EQUIPMENT

Applied Research Laboratories. 1.5-meter grating spectrograph, rotating electrode assembly, 220-volt alternating current spark source, Universal arc-spark stand with cylindrical lens, and densitometer.

CHEMICAL PROCEDURE

Urine Samples. Transfer 50 ml. of recently voided urine to a 250-ml. beaker and add 20 ml. of nitric-perchloric acid mixture. If urine has aged to any extent, acidify in the original container with hydrochloric acid until a clear solution is obtained. Make suitable volume correction for the acid thus added. Cover the beaker and place on a hot plate at medium heat. After the water has evaporated and vapors of nitric oxide are being evolved, increase the temperature of the hot plate just sufficiently to form fumes of perchloric acid, and continue heating until a moist white residue of salts remains. Remove the beaker from the hot plate and allow to cool. This ashing has been found completely satisfactory for all urine encountered to date, and is somewhat less troublesome and time-consuming than other methods of ashing which were tried.

To the cooled beaker add about 25 ml. of distilled water, and warm till all salts are in solution. Transfer the solution and beaker rinsings to a 50-ml. conical tipped centrifuge tube, and add 2 drops of phenol red indicator. By means of a small dropper, add 25% sodium hydroxide solution until the first color change of the indicator is definite and formation of precipitate is imminent. Continue the neutralization with 1% sodium hydroxide solution until 1 drop produces a permanent precipitate. It is not necessary nor desirable to precipitate all the phosphates at this point, for Barnes (*1*) has shown beryllium to be quantitatively precipitated when only a fraction of the total phosphate is precipitated with ammonia; the same has been found true with sodium hydroxide. If too much precipitate is formed, add 1 drop of hydrochloric acid, and repeat the neutralization with dilute sodium hydroxide. Centrifuge for 2 minutes at 2000 to 2500 r.p.m. and decant the supernatant liquid.

Dissolve the precipitate with 1 drop of hydrochloric acid and 25 ml. of hot distilled water, and add 2 drops of phenol red. Stir to dissolve the precipitate completely and add 1 drop of 34% Versene solution. Neutralize to the first appearance of the alkaline red color of the indicator, using 1% sodium hydroxide solution. No precipitate should appear at this point, but should one form, dissolve with a drop of hydrochloric acid, add a drop of Versene solution, and again neutralize as previously directed. Carefully add 1% manganese chloride solution from a buret or dropper, mixing thoroughly after each addition, until the first permanent precipitate persists, as evidenced by a faint turbidity of the solution. Beryllium is satisfactorily collected with the least amount of precipitate detectable, so large precipitates are unnecessary. Centrifuge for at least 5 minutes at 2000 to 2500 r.p.m., or until the supernatant liquid is perfectly clear. Decant as completely as possible, using a filter paper to remove liquid clinging to the tube when inverted.

Add 1 drop of hydrochloride acid and 2.0 ml. of aluminum internal standard solution, and swirl to dissolve the precipitate completely. Particles of silica which may be present do not interfere. The solution is now ready for sparking.

Each series of urines should include a blank specimen, obtained from someone known not to be exposed to beryllium. Standard series are likewise prepared, with appropriate additions of standard beryllium solutions to normal urine.

Air Samples. Air samples are most satisfactorily obtained with an electrostatic precipitator of the type made by the Mine Safety Appliances Co. At the usual sampling rate of 3 cubic feet per minute, a 10-minute sampling period is ample when hygienically significant amounts of beryllium are present in the air, and 20- or 30-minute samples are sufficient for detecting as little as 0.001 microgram of beryllium per cubic meter of air. Filter paper samples may be obtained if desired, but these must first be ashed, and in general offer no compensating advantages. Samples obtained with an electrostatic precipitator are treated as follows.

Rinse the precipitator tube walls with 95% ethyl alcohol from a wash bottle, then scrub with a rubber-tipped glass rod, and repeat this procedure with small rinses until all collected matter is removed, catching the washings in a 100-ml. beaker. Use about 50 ml. of alcohol. Evaporate this solution to dryness, add 5 ml. of 1 to 1 hydrochloric acid, and again evaporate to dryness. To the dry residue add 1 drop of hydrochloric acid and 4.0 ml. of aluminum internal standard, warm gently, and spark a 2.0-ml. aliquot, as directed under spectrographic procedure. Dilute the remaining 2.0 ml. with aluminum internal standard solution if the amount of beryllium present is too great for the usual working curve range.

The above procedure has been satisfactory for all samples which the authors have had occasion to run, but is obviously not satisfactory for the analysis of air samples containing beryllium compounds insoluble in hydrochloric acid. When it is known that such compounds are to be collected, a preliminary fusion or digestion should be performed which is capable of rendering the beryllium soluble, after which the sample may be treated as a urine in order to separate the salts thus acquired.

SPECTROGRAPHIC PROCEDURE

The electrodes are arranged in the ARL rotating electrode assembly as follows.

The upper electrode is a standard 0.25-inch (0.6-cm.) spectrographic carbon of the National Carbon Co., tapered, and with rounded tip. The lower electrode is a graphite wheel 0.5 inch in diameter, 0.1 inch thick, with a hole 0.125 inch in diameter drilled through its center. A graphite rod 0.125 inch in diameter is inserted in the hole until its end is flush with the face of the wheel. The other end of this shaft is inserted into the rotating holder, and adjustment is made to place the wheel directly beneath the upper electrode. The gap is adjusted to 0.15 inch and the lower electrode rotated at 5 r.p.m.

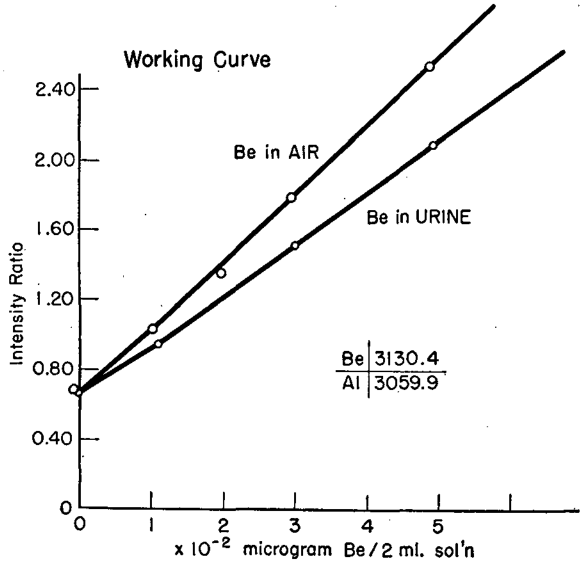

Figure 2. Working Curve

Figure 1 shows a sketch of the assembly. The electrode dimensions have not been found to be critical, and satisfactory wheels may be made by appropriately cutting and drilling 0.5-inch National Carbon Co. electrodes. Wheels thus made should be purified by treating for several days with hot hydrochloric acid, and rinsing thoroughly.

The spark source is set at full inductance, and 85-volt primary voltage. The electrodes are presparked for 55 seconds. The sample solution is then transferred to a small glazed porcelain combustion boat of about 2-ml. capacity, which is placed on the platform beneath the rotating electrode. The platform is raised until the wheel is immersed in the solution as far as possible. The solution is then presparked for 25 seconds, the electrode gap is readjusted, and the film is exposed for a 55-second sparking interval. Another exposure is usually made, although with smaller solution volumes; this can be omitted, if the working curves are made from single exposure ratios.

The densities of Be 3130.4 A. and Al 3059.9 A. are measured on the densitometer, and the ratios determined in the usual manner. Be 3131.2 A. may be used when the amount of beryllium in the solution exceeds about 0.01 microgram, and is the preferred line due to the absence of any background line.

Typical working curves are shown in Figure 2.

Table I. Determination of Beryllium

Be Added, γ	Be Found, γ	% Error
	In Urine[a]	
0.004	0.006	+50
0.005	0.007	+40
	0.007	+40
	Av.	43
0.010	0.010	0
	0.007	−30
	0.011	+10
0.020	0.021	+ 5
0.030	0.034	+13
	0.034	+13
	0.025	−16
0.040	0.035	−13
0.050	0.040	−20
	0.065	+30
	0.047	−6
	Av.	14
	In Air Samples[b]	
0.004	0.003	−25
0.004	0.003	−25
0.005	0.004	−20
	Av.	23
0.010	0.010	0
	0.011	+10
	0.014	+40
	0.009	−10
	0.009	−10
	0.009	−10
0.020	0.019	−5
0.030	0.036	+20
	0.028	−7
	0.028	−7
	0.031	+3
	0.025	−16
0.050	0.052	+4
	0.055	+10
	0.048	−4
	0.048	−4
	0.047	−6
	Av.	10

[a] Total volume of internal standard solution added was 2.0 ml. for all samples.

[b] Total volume of solution sparked was 2.0 ml. for all samples.

RESULTS

Table I summarizes the determination of beryllium in a number of standard urine and air samples which were prepared as described in the procedures; all values were included. It is apparent that greatest accuracy is achieved when the amount of beryllium in the solution being sparked is greater than 0.005 microgram per ml. As shown in Table I, the average error for a urinary analysis is 14% of the amount present on the range 0.005 to 0.025 microgram of beryllium per ml. of solution sparked. Such concentrations correspond to 0.2 to 1.0 microgram of beryllium per liter of urine if a 50-ml. aliquot of urine is used, and the volume of the solution sparked is 2.0 ml. Similarly, if 100 ml. of urine are originally taken, and the final volume of solution sparked is only 1.0 ml., the urinary concentrations would be 0.05 to 0.25 microgram of beryllium per liter. Lesser amounts of beryllium have been determined, down to as little as 0.002 microgram of beryllium per ml. of solution sparked, but such results may be in error by 40 to 50%, as shown.

Greater accuracy is attainable with air samples, for the obvious reason that less manipulations are performed upon the sample. Thus, in the range 0.005 to 0.025 microgram of beryllium per ml. of solution sparked, an average error of 10% is obtained, while in the lower range—i.e., down to 0.002 microgram of beryllium per ml.—the error is about 20% of the amount present. Lesser amounts may still be detected, but accuracy is erratic and uncertain.

DISCUSSION

The isolation of beryllium from urine described by Barnes *et al.* (*1*) appeared to be the most satisfactory starting point. Many samples were run on the dissolved phosphate precipitate obtained by a single precipitation with ammonia. It was evident that the calcium and magnesium phosphate present restricted the lower limit of detection to about 0.4 microgram per liter, and means were therefore sought to extend the sensitivity downward to that attainable with pure beryllium standards. The preferential chelating ability of ethylenediaminetetraacetic acid on calcium and magnesium at a neutral pH appeared promising. Previous work in these laboratories showed this compound to have virtually no chelating power toward beryllium under these conditions. Manganese was chosen to serve as a gathering agent, as it is only moderately complexed by ethylenediaminetetraacetic acid and at the same time yields a gelatinous precipitate with alkali. It was found possible to precipitate a very minute quantity of manganese phosphate by this procedure, which on sparking proved to contain virtually all of the beryllium and yield intensities comparable to those attainable with pure beryllium solutions. Varying amounts of manganese phosphate precipitate do not depress beryllium line intensities.

Of the several metals tried as internal standards, aluminum gave most satisfactory results. A relatively weak reference line of aluminum was chosen to avoid the possibility of error due to extraneous sources of this metal in urine and reagents. No interferences due to manganese or other variables were manifest in this line. What appears to be a water band spectrum presents a faint line at 3130.4 A. This primarily accounts for the failure of blank sample ratios to pass through zero. This background line is sufficiently constant to permit the estimation of beryllium on the concentrations cited. For concentration greater than 0.005 microgram of beryllium per ml., Be 3131.2 A. may be used instead of 3130.4 A. Other beryllium lines may be used for greater concentration than those described, the most useful of which has been found to be Be 2348 A. This line first appears at a concentration of about 0.005 microgram of beryllium per ml.

When it is desired to extend the lower limit of detection of beryllium in urine, 100-ml. samples of urine may be handled if larger centrifuge tubes are used, as difficulty may be experienced in keeping potassium perchlorate in solution. Limiting the final volume of solution sparked to 1 ml. further increases the sensitivity of the method.

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Photometric Determination of Microquantities of Arsenic

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Comparatively few applications of the photometric method for detecting the end points in volumetric determinations have been recorded. No previous use of the ultraviolet region of the spectrum or of the Beckman spectrophotometer has been found for the determination of photometric end points. Ceric ions show a strong absorption band at 320 mμ, whereas cerous, arsenious, and arsenic ions do not absorb at this wave length. With an inexpensive titration cell for use on the Beckman DU spectrophotometer, it is possible to detect the end point photometrically in the titration of microgram quantities of arsenious acid with ceric sulfate. The accuracy of these determinations is 1 to 2 parts per thousand. The preparation and stability of very dilute (10^{-4} N) ceric sulfate solutions have been studied and a method for preparing a solution which is stable for at least 2 months is described. As the photometric determination of the end point in the determination of arsenic with a standard ceric solution eliminates the use of indicators and of indicator errors, and also obviates the necessity of titrating to the exact end point, this method is very accurate and rapid. Use of the ultraviolet region of the spectrum for photometric titrations suggests many more applications of this method.

NUMEROUS applications of the photometric titration principle have been cited in a review by Osburn, Elliot, and Martin (*4*). Later work may be found in the bibliography of a paper by Goddu and Hume (*1*). This work was almost exclusively done with a special commercial photometer. The adaptation of the Coleman Model 14 spectrophotometer for use in photometric titrations was described by Goddu and Hume (*1*).

No previous reference has been found to the use of the ultraviolet region of the spectra for photometric titrations, where the molar extinction coefficients for many volumetric reagents have their maximum value. The application of the ultraviolet region to photometric titrations should lead to a greatly increased sensitivity, better adherence to Beer's law, the use of more dilute volumetric reagents, and a greatly increased number of volumetric reagents which show no strong characteristic absorption in the visible region of the spectrum.

The advantages of working in the ultraviolet region are verified in this paper, where a very dilute ceric(IV) sulfate solution is used for the determination of micro quantities of arsenic.

APPARATUS

The Beckman Model DU spectrophotometer, being one of the most widely used spectrophotometers and having a useful wavelength range of 220 to 1000 mμ, was chosen for this work. The adaptation of this instrument for use in photometric titrations was very simple and inexpensive.

A titration cell was made along the lines described by Goddu and Hume (*1*), except that a rectangular tube (1.8 × 3.0 cm.) was attached to a 200-ml. beaker. The beaker and the upper part of the tube were painted with a flat black; a Bakelite cover was made for the beaker to prevent stray light from reaching the phototube. Two small holes were drilled in the cover, so that a buret and a tube for stirring the solution could be inserted. The solution was mixed within 30 to 45 seconds by employing a stream of carbon dioxide from a very fine orifice. The rectangular tubing of the titration cell was wide enough to allow continuous bubbling of the carbon dioxide without variation of the galvanometer reading, provided the orifice was positioned so that the gas bubbles did not actually enter the light path. The titration cell was positioned in the spectrophotometer by utilizing an extra cell cover into which a slot the size of the tubing was cut. It was necessary to fit this compartment cover with a light-tight felt washer. Using the ordinary hydrogen discharge bulb as the light source, photometric end points at wave lengths as low as 290 mμ were possible with this borosilicate glass cell.

A 10-ml. microburet was used for all the titrations described in this paper. This buret was fitted with a special capillary tip, so that the tip could be kept below the surface of the solution in the titration cell. No appreciable amount of diffusion was observed from this capillary tip in 15 minutes.

PREPARATION OF SOLUTIONS

The preparation of the standard ceric(IV) sulfate solutions was found to be very important for the titrations involving very dilute solutions of this reagent. The difficulties described by Kirk (*2*) were encountered in the titration of arsenic with dilute ceric sulfate solutions prepared in the usual manner. Thus a 0.10 *N* solution which would give very dependable results would often lead to unsatisfactory results when diluted to 1×10^{-3} or 1×10^{-4} *N*. This difficulty was overcome by preparing the very dilute ceric(IV) sulfate solutions by a method similar to that given by Kirk.

The standard stock solution of 0.10271 *N* ceric(IV) sulfate was prepared in the usual manner (*6*), although Kirk's procedure might have been advantageous. This solution was standardized against a standard arsenious acid solution and checked against ferrous ethylenediammine sulfate tetrahydrate. The standardizations with these two reagents checked to within 3 parts per 10,000. In the preparation of the more dilute cerium(IV) solutions it was found that ceric(IV) sulfate as dilute as 4×10^{-4} *N* could be accurately prepared using redistilled sulfuric acid and water with an appropriate aliquot of the standard cerium(IV) stock solution. When 1×10^{-3} *N* ceric(IV) sulfate solution was prepared, the resulting solution was made 2 *N* in sulfuric acid; for 4×10^{-4} *N* cerium(IV) solutions, the solution was only 1 *N* in sulfuric acid. Table I gives the results of the determination of arsenic with the cerium(IV) solutions prepared in this manner.

Table I. Analyses of Arsenic Samples

No. of Detns.	Normality of $Ce(SO_4)_2$	Volume of Solution *Ml.*	Arsenic Taken *Mg.*	Arsenic Found *Mg.*	Average Error %
5	0.10271	150	33.44	33.42	0.11
5	1.0224×10^{-3}	100	0.33286	0.33276	0.09
6	1.0224×10^{-3}	100	0.16630	0.16613	0.10
6	4.106×10^{-4}	75	0.06678	0.06672	0.18

Very dilute ceric(IV) sulfate solutions which were prepared by merely diluting 0.1 *N* cerium(IV) solutions with redistilled sulfuric acid and water were stable for only about 3 days. However, stable solutions of this oxidant could be prepared in the following manner. An appropriate sized aliquot of about 0.1 *N* ceric sulfate was diluted with redistilled sulfuric acid and water to the desired volume and then heated on a steam bath for 7 to 8 hours. The resulting solutions were standardized against a standard arsenious acid solution and it was found that these ceric solutions, when properly protected from dust, etc., were stable for at least 2 months. The results showing the stability of two very dilute ceric solutions are shown in Table II.

The standard arsenious acid was prepared by the usual procedure (*6*). The more dilute arsenious solutions were prepared fresh each day from a standard stock solution (ca. 0.09 *N*) to prevent possible air oxidation.

The 0.01 *M* osmium tetroxide was prepared by the usual method (*6*).

Table II. Stability of Ceric(IV) Sulfate Solutions

Soln. No.	Time of Standing *Days*	Normality of $Ce(SO_4)_2$	Deviation %
1 (2 *N* H_2SO_4)	0	1.007×10^{-3}	
	12	1.0083×10^{-3}	0.13
	28	1.0065×10^{-3}	0.05
	61	1.001×10^{-3}	0.60
2 (1 *N* H_2SO_4)	0	4.0047×10^{-4}	
	10	4.0080×10^{-4}	0.08
	24	3.995×10^{-4}	0.24
	48	4.012×10^{-4}	0.18

EXPERIMENTAL PROCEDURE

The absorption spectrum of ceric(IV) sulfate shows a maximum at approximately 320 mμ, with a molar extinction coefficient of 5.58×10^3 in 1 *N* sulfuric acid (*3*). Thus a wave length of 320 mμ was employed in all titrations with ceric sulfate. Cerium(III) solutions, arsenious acid, and arsenic acid do not absorb appreciably at this wave length.

In the determination of arsenic, a known quantity of a trivalent arsenic solution was added to the titration cell and this solution was then diluted to 100 ml. with sulfuric acid and water, so that the final solution was 1 to 1.2 *N* with sulfuric acid. The actual concentration of the acid was not critical. Three or four drops of 0.01 *M* osmium tetroxide were then added. The slit width of the spectrophotometer was adjusted so that the solution showed zero absorption. Known volumes of the ceric(IV) sulfate solution were added from the microburet and the solution was stirred 30 to 40 seconds before the optical density of the resulting solution was measured. The end point was determined by the usual procedure of plotting absorption against milliliters of ceric(IV) sulfate added. No volume correction was required under any of the reported conditions.

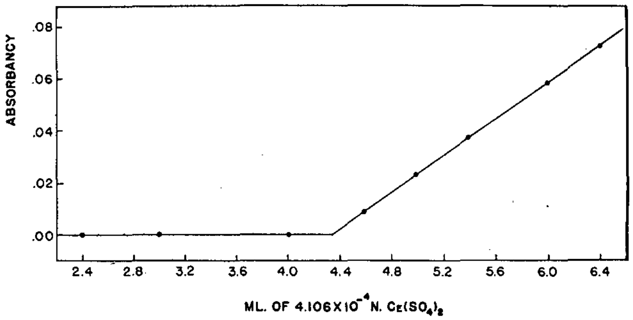

Figure 1. Titration of 66.7 Micrograms of Arsenic in 75 Ml. of Solution with Standard Ceric(IV) Sulfate

The time and tediousness of plotting separate graphs for the end-point determinations were avoided by placing a sheet of linen tracing paper over a piece of graph paper with appropriate labeled ordinates. Thus, readings for an individual titration were plotted on the tracing paper and could be erased quickly after the end point had been obtained.

RESULTS

Figure 1 shows a typical plot of the titration of arsenic with 4.106×10^{-4} *N* ceric sulfate solution. In most titrations with arsenic, the optical density prior to the end point may be taken as zero in the plots without appreciable error. Four to six points were taken after the end point, although fewer points could be used when slightly less accuracy was permissible.

It is apparent from the results shown in Table I that various concentrations of standard ceric sulfate can be used with comparable accuracy in the photometric titration of arsenious acid. These results do not show the minimum amount of arsenic that may be determined by this method. By the use of smaller volumes, a smaller buret, and more dilute ceric sulfate solutions, it should be possible to determine considerably smaller amounts of arsenic with a reasonable degree of accuracy.

Ceric(IV) sulfate solutions as dilute as 1×10^{-3} and 4×10^{-4} N can be prepared which show only small changes, if any, in normality over a period of 2 months.

Further application of the use of dilute ceric solutions for photometric titrations is in progress. Preliminary work by the authors would indicate that the range of usefulness of dilute ceric solutions in photometric titrations could be extended by increasing the oxidation potential of the cerium(IV) by the use of perchloratocerate. The application of very dilute perchloratocerate solutions using nitroferroin indicator to the determination of calcium in blood plasma and to the microdetermination of arsenic and iron has been described by Smith and coworkers (*5*, *7*). The use of hydrochloric acid in the ceric sulfate titrations is not possible because of the rapid oxidation of the chloride ion when excess cerium(IV) is present. However, in the presence of excess sulfuric acid, significant amounts of chloride ion can be tolerated.

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NOTES ON ANALYTICAL PROCEDURES . . .

Determination of Free Carbon in Atmospheric Dust

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THE soiling property of atmospheric dust is of major economic importance in heavily populated areas. Because this property is due to a considerable extent to the proportion of free carbon present, design and test studies in the air cleaning industry have made necessary the development of a convenient analytical method for the determination of free carbon in this dust.

METHOD

The sample is treated with 70% nitric acid and heated to destroy the organic matter. The residue which contains the free carbon and insoluble inorganic matter is collected in a porcelain filter crucible, dried, and weighed. Free carbon is then determined by the loss of weight of the crucible on ignition.

Procedure. Duplicate samples of 0.2 to 0.8 gram are weighed into 250-ml. beakers and 25 ml. of 70% nitric acid are added. Small samples are desirable with material of high free carbon content. The mixture is covered with a watch glass and boiled for 20 minutes, diluted with 125 ml. of 6 N nitric acid, and allowed to stand overnight. (It is necessary that the supernatant liquid be strongly acid, or the carbon will become dispersed and be impossible to separate by filtration.) The supernatant liquid is carefully decanted through a tared porcelain filter crucible and the insoluble material collected. The crucibles and contents are dried for 2 hours at 140° C., cooled, and weighed; then they are ignited for 2 hours at 700° C., cooled, and weighed; the loss in weight is free carbon.

Table I. Digestion of Carbon Black with 70% Nitric Acid

Free Carbon Taken *Gram*	Free Carbon Found *Gram*	Difference *Gram*	Time Digested *Min.*
0.5897	0.5906	+0.0009	15
0.3249	0.3253	+0.0004	30
0.3421	0.3422	+0.0001	45
0.3374	0.3381	+0.0007	60
0.3405	0.3419	+0.0014	75
0.3063	0.3080	+0.0017	90

DISCUSSION

Atmospheric dust contains organic matter, inorganic matter, and free carbon. The organic matter, largely lint, is easily destroyed by wet oxidation with nitric acid. Part of the inorganic matter is dissolved by the nitric acid, and the insoluble portion is collected with the free carbon. The free carbon is the loss of weight occurring when the inorganic matter and free carbon collected are ignited.

The wet-oxidation technique of determining free carbon in rubber products is a standard procedure in the rubber industry (*1*, *2*), where the treatment necessary to degrade the rubber polymer yielded high results, at first attributed to the formation of graphitic acids (*2*) but now considered due to insufficient drying (*3*). The analytical method outlined in this paper is not seriously affected by this error (Tables I and II).

To test the validity of the proposed analytical method, the

Table II. Digestion of Synthetic Mixtures with 70% Nitric Acid

Free Carbon Taken *Gram*	Free Carbon Found *Gram*	Difference *Gram*
Composition, 70% wood flour, 20% SiO_2, 10% free carbon		
0.1077	0.1080	+0.0003
0.1081	0.1067	−0.0014
0.1012	0.1001	−0.0011
0.1055	0.1047	−0.0008
0.1135	0.1133	−0.0002
Composition, 25% wood flour, 25% SiO_2, 50% carbon		
0.5432	0.5435	+0.0003
0.4339	0.4343	+0.0004
0.4730	0.4745	+0.0015
0.5358	0.5360	+0.0002
0.4691	0.4692	+0.0001
Composition, 10% wood flour, 70% SiO_2, 20% carbon		
0.2282	0.2276	−0.0006
0.2384	0.2386	+0.0002
0.2048	0.2046	−0.0002
0.2041	0.2036	−0.0005
0.2099	0.2105	+0.0006
Composition, 10% wood flour, 10% SiO_2, 80% carbon		
0.9051	0.9032	−0.0019
0.9016	0.9012	−0.0004
0.9127	0.9127	±0.0000
0.8400	0.8406	+0.0006
0.8735	0.8744	+0.0009

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Table III. Free Carbon in Samples Collected over Some American Cities

Location	Remarks	Free Carbon %
Boston, Mass.	Near center of business district	46.5
Pittsburgh, Pa.	Near industrial and business section	36.0
Pittsburgh, Pa.	Poor residential area	46.7
Pittsburgh, Pa.	Good residential area	34.0
Tulsa, Okla.	Business district	8.0

effect of the nitric acid digestion on standard carbon black was determined (Table I) and synthetic dirt samples of approximately the chemical composition of atmospheric dust were prepared from standard test materials in the air cleaning field—wood flour (organic material), silica (inorganic material), and carbon black (free carbon) (Table II).

Under conditions where high concentrations of clay are probable, the method should be used with caution, as the water lost during ignition would lead to high results. Samples containing a high proportion of organic matter may need longer digestion. The completion of the digestion can be determined by the disappearance of the gelatinous particles that adhere to the sides of the beaker.

Representative results obtained from samples collected in a number of urban areas are shown in Table III.

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Separation of 2,4-Dinitrophenylhydrazones of Some Substituted Benzaldehydes by Chromatographic Adsorption

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THERE have appeared many modifications of the process introduced by Strain (*16*) in 1935 for the separation and purification by chromatographic methods of the 2,4-dinitrophenylhydrazones of carbonyl compounds. Subsequent workers used a variety of adsorbents: activated alumina (*2*, *4*, *6*, *7*, *10–12*), silicic acid (*5*, *14*), Florisil and alumina (*18*), magnesium sulfate (*1*, *15*, *19*), bentonite (*20*), zinc carbonate (*17*), filter paper (*3*, *13*), filter paper containing silicic acid (*8*), and acetylated paper (*9*).

The hydroxy- and alkoxybenzaldehydes form a group of compounds of great interest, which includes many of the ingredients of naturally occurring flavors and odors. Some of these compounds, especially vanillin and syringaldehyde, are closely related to lignin and are frequently encountered in wood products. The 2,4-dinitrophenylhydrazones of a few individuals of this group have been included in previous publications on chromatography (*13*, *16*). However, no systematic study of a representative number of the 2,4-dinitrophenylhydrazones of these aldehydes, similar to White's (*20*) study of aliphatic 2,4-dinitrophenylhydrazones, has previously been reported.

In the present work, the adsorption of the 2,4-dinitrophenylhydrazones of twelve substituted benzaldehydes containing one or more hydroxyl, methoxyl, or ethoxyl groups was investigated. Also included in this study were benzaldehyde 2,4-dinitrophenylhydrazone and the reagent 2,4-dinitrophenylhydrazine, which must be considered as a possible impurity whenever a 2,4-dinitrophenylhydrazone is prepared. The adsorbent selected was a uniform mixture of silicic acid and Celite. This adsorbent is sufficiently active to separate the two least readily adsorbed 2,4-dinitrophenylhydrazones and yet it permits elution of the most actively adsorbed 2,4-dinitrophenylhydrazones. Pure benzene proved satisfactory as the solvent both for adsorption and for development of the chromatogram. The single unmixed solvent has the advantage that it avoids the possibility of erroneous results due to improper selection of solvent mixtures. Furthermore, the recovered benzene may be easily purified and re-used.

EXPERIMENTAL

Materials. The adsorbent mixture consisted of 1.5 parts by weight of Merck reagent silicic acid mixed thoroughly with 1 part of Johns-Manville Celite No. 545. Both powders were used as received from the manufacturer. (One lot of silicic acid which had been stored for 6 months, including an extremely humid summer, required heating for 1 hour at 110° C. before it could be used satisfactorily.) Columns were conveniently prepared from lengths of glass tubing 5 mm. in inside diameter. The adsorbent was retained by a glass wool plug and was firmly tamped into place to a column height of 16 cm. Columns prepared in this manner permitted the separation of adsorption zones by the simple procedure of cutting the column between zones, removing the adsorbent, and eluting the corresponding 2, 4-dinitrophenylhydrazones. When it was necessary to utilize larger quantities, a column 18 × 125 mm. was used without affecting the adsorption characteristics of the dinitrophenylhydrazones investigated. The quantities employed with the two sizes of columns were 20 to 75 micrograms for the small columns and approximately 15 times these quantities for the larger columns.

Procedure. The adsorbent in the column was first washed with 3 volumes of benzene; then the sample, consisting of a mixture of saturated benzene solutions of 2, 4-dinitrophenylhydrazones (from 0.02 ml. of the least actively adsorbed compound studied to 3 ml. of the most actively adsorbed 2, 4-dinitrophenylhydrazones) was introduced. Additional benzene was passed through the column until separation of the zones occurred or until the sample was eluted. Moderate vacuum was applied throughout the run. The zones were separately eluted from the column with additional solvent. In some cases, the column was cut as described above; the 2,4-dinitrophenylhydrazones were eluted with chloroform containing 5% ethyl alcohol and were recovered by evaporation of the solvent.

All binary combinations of the fourteen compounds studied were tested for separation, which was considered to be satisfactory when two distinct, isolated zones appeared on the column or in the eluate. Separation was classed as incomplete when the two observable zones overlapped or when a single zone could be shown, by sectioning or fractional elution, to differ appreciably in the 2,4-dinitrophenylhydrazone proportions in the leading and trailing edges. From the results, the substances were listed in the order of decreasing adsorbability. Finally, all combinations of three substances placed in sequence on the list were investigated for separability in the same manner.

Methods of Identifying Zones. Several methods were used to identify the separate zones which appeared on the columns.

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Figure 1. Chromatographic Separation of Binary Combinations of 2,4-Dinitrophenylhydrazones of Thirteen Substituted Benzaldehydes and 2,4-Dinitrophenylhydrazine

		Syringaldehyde B	*p*-Hydroxybenzaldehyde C	Veratraldehyde D	*m*-Hydroxybenzaldehyde E	2,4-Dinitrophenylhydrazine F	Vanillin G	2-Hydroxy-3-methoxybenzaldehyde H	Ethylvanillin I	Anisaldehyde J	*m*-Methoxybenzaldehyde K	Salicylaldehyde L	*o*-Methoxybenzaldehyde M	Benzaldehyde N
Protocatechualdehyde	A													
Syringaldehyde	B													
p-Hydroxybenzaldehyde	C			P	P									
Veratraldehyde	D				P	P								
m-Hydroxybenzaldehyde	E					P								
2,4-Dinitrophenylhydrazine	F						P	P						
Vanillin	G							X	P					
2-Hydroxy-3-methoxybenzaldehyde	H								X					
Ethylvanillin	I													
Anisaldehyde	J										P	P		
m-Methoxybenzaldehyde	K											P		
Salicylaldehyde	L												P	
o-Methoxybenzaldehyde	M													
Benzaldehyde	N													

Legend: ☐ Satisfactory separation P Incomplete separation X No separation

Estimation of the quantity of 2,4-dinitrophenylhydrazone, by accomplishing two similar separations with widely different amounts of each 2,4-dinitrophenylhydrazone—viz., 2 volumes of A plus 1 volume of B, and 1 volume of A plus 2 volumes of B. The relative positions of A and B were then apparent from the depth and color intensity of the zones in the parallel runs.

Color of the eluted and recovered solid 2,4-dinitrophenylhydrazone.

Color produced by dissolving the recovered 2,4-dinitrophenylhydrazone in alcoholic alkali (*15*). A significant range of colors was obtained with the 2,4-dinitrophenylhydrazones investigated. It was possible to distinguish between the members of many pairs by the distinct differences in color produced in this test.

Adsorption on activated alumina. 2,4-Dinitrophenylhydrazones containing a phenolic hydroxyl group adsorb on alumina much more firmly than do the other 2,4-dinitrophenylhydrazones. It is thus possible to distinguish between 2,4-dinitrophenylhydrazones of phenolic and nonphenolic benzaldehydes in an isolated chromatographic zone.

Melting point of the recovered 2,4-dinitrophenylhydrazone. This method required more sample and, therefore, larger columns than did the other methods. It was not utilized when clear identification resulted from the other methods.

RESULTS AND DISCUSSION

The results of chromatographing all binary combinations of the 14 dinitrophenylhydrazine derivatives are presented in Figure 1, in which the 2,4-dinitrophenylhydrazones are listed in the order of decreasing strength of adsorption. Of the 91 pairs studied, 2 pairs gave no evidence of separation, 12 pairs separated incompletely, and 77 pairs separated satisfactorily.

Chromatographic separations were attempted of all combinations of three substances which appear in sequence in Figure 1. In the following tabulation of results obtained, each compound is designated by the letter symbol that appears with it in Figure 1. The letters within each pair of brackets signify that the corresponding compounds formed a single chromatographic zone. Zones containing more than one 2,4-dinitrophenylhydrazone were not examined for partial separation, as the object of this portion of the investigation was a simple estimation of the applicability of the described technique to the analysis of unknown mixtures of more than two of these compounds.

[A] + [B] + [C]
[B] + [C + D]
[C + D + E]
[D + E + F]
[E + F + G]
[F + G + H]
[G + H + I]
[H + I] + [J]
[I] + [J + K]
[J + K + L]
[K + L + M]
[L + M] + [N]

The results followed a pattern that could be predicted from the results obtained with binary mixtures. Thus, in the case of the trio E, F, and G, neither pair E and F nor pair F and G separated, although pair E and G did; therefore, separation of the ternary mixture did not occur.

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Mass Spectrometric Determination of Oxygen in Water Samples

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A WIDELY used procedure for the mass spectrometric isotopic determination of oxygen in water samples is that of Cohn and Urey (*3*). Carbon dioxide is equilibrated with a liquid water sample and is then introduced into the mass spectrometer. From the ratio of mass peaks 44 and 46 ($CO^{16}O^{16}$ and $CO^{16}O^{18}$) and the equilibrium constant for the carbon dioxide–water exchange reaction, the atom percentage of O^{18} in the sample may be calculated. One disadvantage of this method is the length of time required for the completion of the equilibration process, from 4 to 12 hours.

The authors have modified the original method of Cohn and Urey by carrying out the equilibration reaction on a heated platinum wire placed in a gaseous mixture of the two components. The equilibrium under these conditions is complete within a few minutes. The apparatus used for the equilibration is shown on Figure 1, and was constructed as an integral part of the gas inlet system of the authors' mass spectrometer.

The equilibrium vessel, *A*, consists of a cylindrical borosilicate glass bulb of 100-ml. capacity fitted with a vacuum stopcock, *B*, at its lower end and carrying a re-entrant thimble at the other. Around this thimble, and supported by small platinum hooks projecting from it, is arranged a platinum wire, 25 cm. long and 0.2 mm. in diameter, in a manner analogous to that used in some early incandescent lamps. A hairpin bend at the bottom of the platinum loop is provided to ensure that no liquid water remains in the stopcock opening. The only other component of the system which needs special mention is the sample-introducing and -removing stopcock, *C*, which was made from a vacuum T-shape hollow-plug stopcock provided with a dosing cavity. A 10/30 standard taper socket was sealed to it. To minimize memory effects, the lengths of tubing between the components *B*, *C*, and *D* were kept as short as possible.

Table I. Mass Spectrometric Determination of O^{18} in Samples of Water

Sample No.	Expt. No.	Ratio Peaks 44/46, Dostrovsky and Klein	Mean	Enrichment	Ratio Peaks 44/46, Cohn and Urey	Mean	Enrichment
A	1	22.4			23.1		
	2	23.1			21.8		
	3	22.6	22.7	10.56	22.6	22.5	10.42
B	1	36.7			35.4		
	2	36.7			36.1		
	3	36.2	36.5	6.57	35.9	35.8	6.55
C	1	62.7			62.0		
	2	64.0	63.2	3.77	63.6	62.8	3.71
D	1	220					
	2	221			214		
	3	217			210		
	4	224	220	(1.0)	221	215	(1.0)

Procedure. The apparatus is evacuated thoroughly through stopcock *D* and the equilibrium vessel is baked for a few minutes by heating the platinum wire to red heat. With the heating current off, liquid air is introduced into the thimble. The sample of water (20 mg.) is then introduced into the dosing cavity of *C*, with the aid of a micrometer syringe. This quantity of water is sufficient to fill the cavity almost completely. Stopcock *C* is then turned so as to expose the cavity to the vacuum, whereupon the water distills onto the cooled thimble. Stopcock *B* is then turned off and purified carbon dioxide from a storage flask is introduced through *D* until a predetermined pressure is indicated on the manometer, *M*. The quantity of carbon dioxide introduced was equivalent to about 1.5 ml. at normal temperature and pressure. The gas is introduced into *A* by opening *B* momentarily and the liquid air remaining in the thimble is removed by blowing some air through it. The filament is then switched on and the current regulated so as to maintain the wire at bright red heat, varying the current with changes of pressure in *A*.

Two minutes after all traces of liquid water have disappeared from the walls of the vessel, stopcock *C* is turned so as to connect a small trap, *T*, which is attached to *C*. The trap is immersed in liquid air and all the material condensed in it by opening stopcock *B*. After pumping out, the apparatus is ready for the next sample, which may be introduced while the reaction products are still frozen in *T*. While the equilibration of the fresh sample is taking place, with stopcock *B* off, sampling stopcock *C* is turned to connect *T* with the apparatus and the contents of the trap are allowed to warm up. As soon as the rapid evolution of gas ceases (as indicated by the manometer), *C* is turned through 90° and the carbon dioxide is introduced into the mass spectrometer sampling line through *D*. The water in *T* may be recovered if required, but in any case *T* is replaced by a clean dry trap in readiness for the next sample.

This procedure permits a complete analysis to be made in under 15 minutes and a large number of samples can be treated in rapid succession. In Table I are collected some of the results obtained by this procedure, compared with results obtained on the same samples by the original procedure of Cohn and Urey.

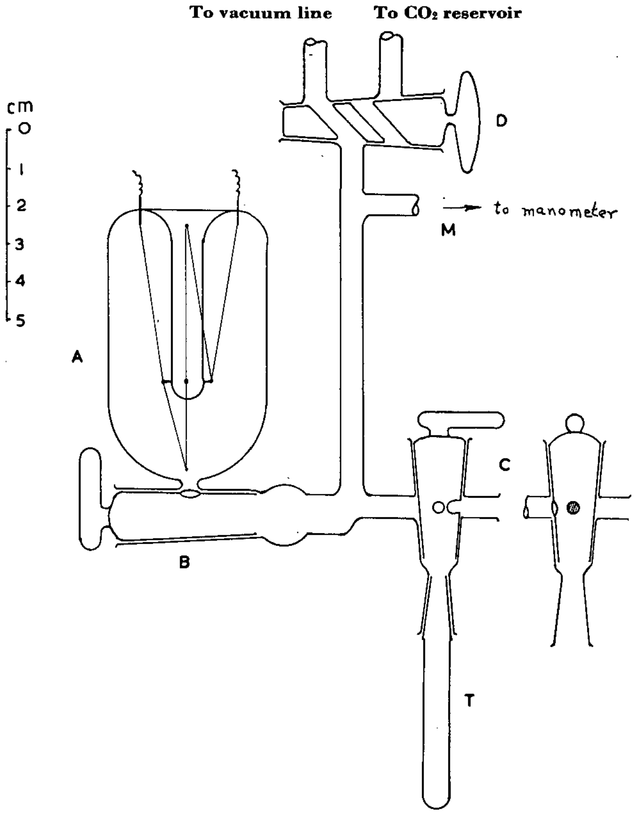

Figure 1. Apparatus

In the course of the equilibration reaction a certain dilution of the sample by the carbon dioxide oxygen atoms occurs. The concentration of O^{18} in the water sample may be calculated readily from the observed ratio of peaks 44 and 46 by means of Equation 5.

The relevant equilibrium constants in the equilibration reaction are:

$$\frac{(H_2O^{16})(CO^{16}O^{18})}{(H_2O^{18})(CO_2^{16})} = K \qquad (1)$$

$$\frac{(CO^{16}O^{18})^2}{(CO_2^{16})(CO_2^{18})} = 4 \qquad (2)$$

Table II. Ratio Peaks

Sample Sequence	Ratio Peaks 44/46	Apparent Dilution by Previous Sample, %
Sample A	22.4	
Normal water	189	1.9
Limiting value for normal water	220	
Sample B	36.7	
Normal water	198.5	2.2

and by definition

$$\frac{(CO_2^{16})}{(CO^{16}O^{18})} = R \tag{3}$$

(assuming equal sensitivity of spectrometer to CO_2^{16} and $CO^{16}O^{18}$ molecules).

From consideration of material balance it follows that:

$$a(N_0 - N_e) = 2b(n_e - n_0) \tag{4}$$

where N_0 and N_e are the atom fractions of O^{18} in the water sample before and after equilibration, respectively; n_0 and n_e are the corresponding quantities for carbon dioxide.

a and b are the number of millimoles of water and carbon dioxide, respectively, taken for analysis.

R_0 and R_e are the ratios of mass peaks 44 to 46 for carbon dioxide before and after equilibrium, respectively.

From Equations 1 and 3 it follows readily that

$$N_e = \frac{1}{KR_e + 1}$$

and from Equations 2 and 3 similarly $n = \frac{1}{2(R + 1/2)}$

Introducing these values into Equation 4 we obtain:

$$N_0 = \frac{1}{KR_e + 1} + \frac{b}{a}\left(\frac{1}{R_e + 1/2} - \frac{1}{R_0 + 1/2}\right) \tag{5}$$

In using Equation 5, for K the value of 2.005 is taken for equilibration by the authors' method when the temperature is near 1000° K., and 2.076 for the room temperature equilibration by the method of Cohn and Urey.

The equation used here, even without the dilution-correcting term, differs from the equation given for this analysis by Bentley (*1, 2*) which contains algebraic errors.

The enrichments (columns 5 and 8 of Table I) were obtained by dividing the atomic fraction calculated from Equation 5 by the value of the concentration of normal water obtained experimentally in a similar way. This procedure was adopted to minimize the effect of any systematic errors on the value of the enrichment.

The apparatus possesses a small memory effect. If a normal water sample be analyzed immediately after a concentrated one, the peak ratio will be found somewhat lower than normal. This effect is probably due to traces of water or carbon dioxide absorbed on the surface of the glass and possibly also due to exchange with the glass oxygen atoms. The magnitude of this effect is illustrated in Table II.

It was found convenient to wipe out memory effect in switching between samples of widely different isotopic composition by flushing the apparatus with the new sample once or twice before admitting the equilibrated gas to the mass spectrometer. In general, the work is planned in such a manner as to avoid measuring samples of extreme concentration difference in succession. By careful work, giving more time to baking out and pumping, it is possible to reduce the memory effect well below the figures in Table II.

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Rapid Determination of Organic Acids in Cured Tobacco

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THE usual method for determining organic acids in plant material by the technique of Pucher, Vickery, and Wakeman (*2*) is time-consuming and subject to considerable experimental error. Isherwood (*1*) has used partition chromatography to determine organic acids in apple tissues. The organic acids are extracted from a tissue sample with an appropriate solvent and the extract is concentrated to a small volume. An aliquot is then placed at the top of a specially prepared column of silica gel and the acids are washed down the column with a mixture of 1-butanol and chloroform. An external indicator is used to determine when an acid is emerging from the column, and it also indicates when the acid has been completely washed through. As the different organic acids travel down the column at different rates, it is possible to collect them in separate fractions and thus determine the amounts of each acid by a simple titration procedure.

Certain modifications of Isherwood's technique provide a simple and accurate method for the rapid determination of oxalic, malic, and citric acids in dry plant materials such as cured tobacco leaves.

EXPERIMENTAL

By placing the acidified sample of tissue at the top of the column, the extraction and partitioning are made to occur simultaneously, thus eliminating the necessity for concentrating a large volume of extract. This also makes possible the use of a smaller sample of material for analysis. Sharpness of the separations depends upon selection of a proper size of sample and judicious manipulation of the two solvent mixtures used.

For cured tobacco the two solvent mixtures that gave best separations over a wide range of total organic acid concentrations were 15 and 30% (v./v.) 1-butanol in chloroform. The solvents were saturated with 0.5 *N* sulfuric acid, stored in large reservoirs, and delivered to the chromatograph columns under about 5 pounds of air pressure.

Delivery of the solvents through two-way pressure stopcocks attached to the columns permits ready interchange of solvents on a column and simultaneous analysis of several samples. The setup used in this laboratory is designed to accommodate six columns.

The column is a borosilicate glass tube 13 mm. in internal diameter and 300 mm. long with indentations near the bottom to support a perforated aluminum disk which is covered with filter paper and a small plug of cotton. A capillary tube drawn to a fine tip and provided with a grooved stopcock is used to control the flow of external indicator from a large reservoir. A small funnel about 50 mm. in diameter and with a stem about 150 mm. long is bent near the base of the cone, so that the major portion of the stem is horizontal and its tip is turned down. The funnel is plugged at the bottom of the cone with a small twist of glass wool, which provides an efficient chamber for mixing the external indicator and effluent solvent. The funnel is placed under the column, so that it receives the effluent. The color of the emulsion is noted as it travels the horizontal portion of the stem. By properly fitting the glass wool, a good emulsion can be obtained which makes it possible to observe the precise end point of one acid fraction and the beginning of the next.

PROCEDURE

The material to be analyzed is ground to pass a 100-mesh screen and thoroughly mixed. A sample containing 0.2 to 0.4 me. of total organic acids is taken for analysis. Usually 0.1 gram of cured tobacco is sufficient. In this case 0.4 ml. of 4 *N* sulfuric acid is added and thoroughly mixed with the sample in a small beaker. To this mixture 0.3 gram of silica gel, prepared according to Isherwood, is added and stirred until the whole appears to be a dry powder.

Three grams of silica gel are mixed with 3 ml. of 0.5 *N* sulfuric acid and suspended in 25 to 30 ml. of the 15% solvent. The suspension is poured into the chromatograph tube and the excess solvent forced out with gentle air pressure until the solvent level just disappears below the top of the silica gel.

The prepared sample in the beaker is suspended in about 5 ml. of the 15% solvent and transferred to the top of the silica gel column. The beaker is then rinsed two or three times with small amounts of solvent and finally wiped clean with a small plug of cotton, which is pushed down into the chromatograph tube until it rests on the sample. The column is filled with the 15% solvent and connected with the solvent reservoirs through the two-way pressure stopcock. External indicator, 0.02% solution of thymol blue prepared according to Isherwood, is permitted to flow at the rate of about 1 drop per 10 drops of solvent emerging from the column. The 15% solvent is forced through the column under about 5 pounds' air pressure until the oxalic acid fraction is completely washed through. Two very small acid fractions precede the oxalic acid fraction in most cured tobacco samples. The stopcock is then adjusted to force the 30% solvent through the column until all of the malic acid and citric acid fractions are collected. If the sample is unusually high in citric acid, better separation of malic and citric acids is obtained if the 15% solvent is forced through until all the malic has been collected.

The acid fractions are titrated with 0.01 *N* barium hydroxide. During the titration the solvent and water mixture is shaken vigorously, and as the end point is approached the two layers are allowed to separate for observation. Barium hydroxide has less tendency to form stable emulsions under these conditions than either sodium or potassium hydroxide. An excess of 0.01 *N* barium hydroxide is added and the mixture is back-titrated with 0.01 *N* hydrochloric acid until the chloroform-butanol layer is definitely pink.

Table I. Recovery Tests

	C.P. Acids Alone, Me.		0.05 Gram of Cured Tobacco, Me.			%
				Plus C.P. Acids		
	Added	Found	Alone	Added	Found	Recovery
Oxalic	0.112	0.116	0.023	0.079	0.080	101.3
Malic	0.075	0.072	0.024	0.061	0.059	96.7
Citric	0.078	0.076	0.073	0.112	0.110	98.2
Total	0.265	0.264	0.120	0.252	0.249	98.8

Table II. Reproducibility Tests

Lab. No.	Acids Found in 0.1 Gram Samples of Cured Tobacco, Me.					
	Unknown 1	Unknown 2	Oxalic	Malic	Citric	Total
2	0.008	0.005	0.046	0.054	0.130	0.293
	0.008	0.004	0.044	0.056	0.131	0.293
73	0.004	...	0.047	0.031	0.050	0.132
	0.004	...	0.049	0.034	0.050	0.137
3	0.011	0.004	0.073	0.041	0.100	0.229
	0.010	0.004	0.073	0.044	0.098	0.229
67	0.008	...	0.066	0.020	0.058	0.152
	0.008	...	0.064	0.020	0.058	0.152
75	0.007	0.003	0.059	0.029	0.086	0.180
	0.006	0.004	0.054	0.027	0.089	0.184

An examination of Tables I and II indicates the accuracy and precision to be expected with this technique. Fair precision is obtainable when as little as 0.004 me. of an acid is present. The limiting factor in the upper range is the ability of the column to separate large acid fractions, but generally the best separations on the size of column described here are obtained when the quantity of the total acids does not exceed 0.4 me.

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Technique for Noting Combustion in Oxygen Bombs

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CERTAIN widely used oxygen bomb methods for sulfur and chlorine (*1*) specify the ignition of the sample charge in a platinum cup by means of nylon thread or absorbent cotton supported on a platinum firing wire. Passage of current through the firing wire is regulated so as to ignite the nylon or cotton and thus the oil sample without melting the wire.

Ignition in platinum and eliminating the use of iron fuse wire avoid contamination by iron oxide, but ignition by this procedure sometimes fails because the magnitude of the current may be too low to ignite the nylon or cotton. In such a case it is necessary to try the ignition again, still keeping the current low enough that the platinum wire is not melted.

Determination of firing or of failure to fire has been made by placing the hand on the outside of the bomb and noticing the rise or lack of rise in temperature. This is not considered a safe practice because the operator is exposed to the chance of a ruptured bomb at the time of its peak pressure development.

A very simple method of quickly checking the firing consists of attaching a small thermocouple to the side of the bomb and noting the deflection of a suitable potentiometer or millivoltmeter as the surface temperature increases. Even when the bomb is immersed in ice water a definite deflection is obtained.

The procedure used in these laboratories for the past several months is as follows:

The bomb (Parr Instrument Co. double valve, Model 1101) is charged with up to 0.8 gram of sample and oxygen to a pressure of 35 atmospheres. A heavy rubber band is tightly stretched around the bomb cylinder and the bead of an iron-constantan thermocouple, B. & S. gage 22, is thrust under the band to effect firm contact with the bomb cylinder. Leads from a variable transformer, set to a predetermined voltage, are attached and the bomb is placed in a small pail of ice water. This in turn is placed inside a steel shield consisting of a 13-inch length of 12-inch steel pipe which stands vertically on a circular steel plate to which it has been welded. The e.m.f. developed by the thermocouple is balanced by a portable L. & N. potentiometer without regard to its actual value. The preselected current is passed through the bomb for an appropriate interval—e.g., 4 seconds—and if firing occurs this is shown by a definite deflection. Typically, the deflection may be 5 scale divisions, corresponding to approximately 0.5 to 1.0 millivolt, roughly equivalent to 10° to 20° C.

Should the lack of voltage change indicate a failure to ignite the sample, a further effort can be made promptly by adjusting time or magnitude of current without removing the bomb from its water bath and protecting cylinder.

The convenience with which repeated combustion efforts can be made encourages the use of moderate firing currents and has decreased the number of melted firing wires.

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Rapid Volume and Concentration Calculations in Industrial Air Analysis

Slide Rule Technique

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THE wet-test meter is generally used for measuring large sample volumes in analysis of industrial air. The volume of a gas indicated by such a test meter under sampling conditions of temperature and pressure is not truly representative of the quantity of matter present and, for comparison with succeeding measurements, must be adjusted to an arbitrarily defined standard temperature and pressure. These standards vary among laboratories, but standard temperature is generally in the range of 20° to 30° C. and standard pressure is usually 760 mm. of mercury on a dry basis.

An equation combining the laws of Charles and Boyle is generally used for this correction, but it contains four variables and may not be put too readily or compactly into table form. Barr (*1*) has proposed a nomogram for reducing gas volumes to normal temperature and pressure, while Patton (*3*) has proposed a chart for reducing volumes to standard temperature and pressure. Roof (*4*) has suggested a pair of nomograms for correcting volumes of gases over small ranges of temperature and over any range of pressure. The present paper describes a slide rule designed to correct gas volumes to 25° C. and 760 mm. of mercury pressure with accuracy sufficient for industrial control purposes. The design may easily be altered to allow correction to any temperature and pressure desired. Additionally, the method may be adapted to calculations relating parts per million by volume of most industrial air contaminants retained after sampling in absorbing medium to the volume of standard reagent used to titrate, directly or indirectly, the contaminant in the absorbing medium.

The Boyle-Charles law may be expressed as

$$Vc = Vo \times \frac{Pc}{Ps} \times \frac{Ts}{To} \qquad (1)$$

where Vc = corrected volume, liters
Vo = observed volume, liters
Pc = atmospheric pressure less water vapor pressure, mm. of mercury
Ps = standard pressure, mm. of mercury
Ts = standard temperature, ° A.
To = observed temperature, ° A.

If standard conditions are chosen as 25° C. and 760 mm. of mercury, this equation may be rearranged to

$$\frac{Vc}{Vo} = \frac{298}{760} \times \frac{Pc}{To} = 0.392 \times \frac{Pc}{To} \qquad (2)$$

By taking the logarithm of Equation 2

$$\text{Log } Vc - \log Vo = \log (0.392Pc) - \log To \qquad (3)$$

here results an equation of the form

$$f_1(a) - f_2(b) = f_3(c) - f_4(d) \qquad (4)$$

which may be expressed as a nomogram (*2*).

Two pairs of axes, *Vc* and *Vo*, *Pc* and *To*, are constructed on the log scale of single-cycle semilog paper. The distance between *Pc* and *To* is made equal to that between *Vc* and *Vo* and any convenient space is left between the two pairs. Identical linear units must be used for each pair. It is convenient to plot volumes between 10 and 100 liters, although a different range or volume unit is permissible as long as the logarithmic aspect of the scale is maintained. Pressures are plotted as the product 0.392 *Pc* but are marked on the scale as *Pc*—i.e., *Pc* of 760 mm. would be plotted as 0.392 × 760 = 297 on the scale but would be marked as 760. Temperatures are plotted as ° A. but are marked as ° C.—i.e., 27° C. would be plotted as 273 + 27 = 300° A. but would be marked as 27° C.

The nomogram (Figure 1) may be operated for a given set of experimental conditions by connecting given *Vo* and *To* values by a straight line. Then, a line parallel to the first is passed through the given point, *Pc*. The point of intersection of the latter line with the axis, *Vc*, gives the required value of the corrected volume.

Figure 1 shows that this nomogram is admirably adapted to use as a slide rule if the *Vc* and *Vo* scales are made the outside, stationary scales and the *Pc* and *To* scales are placed on the slide. By aligning the required values on the *Vo* and *To* scales, the *Vc* value may be observed opposite the known *Pc* value.

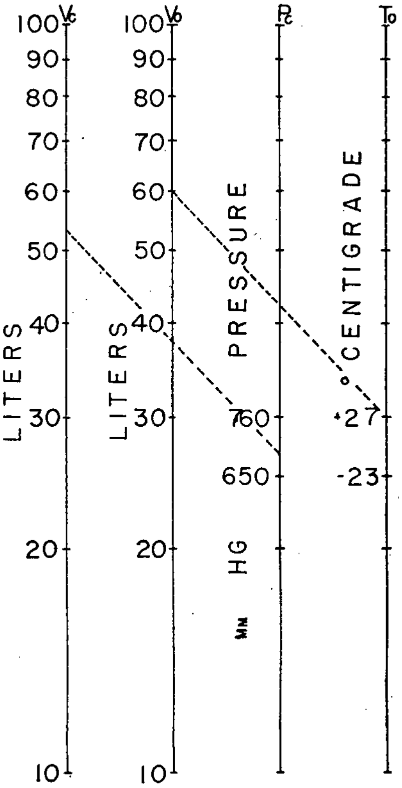

Figure 1. Nomogram

Although the rule, as described, will correct volumes only to a standard of 25° C. and 760 mm. of mercury, correction to any desired standard may be achieved by varying the values of *Ps* and *Ts* in Equations 1 and 2.

Most chemical analyses of air consist of drawing the sample air through a liquid absorption medium and either titrating the absorbed air contaminants directly with standard titrant or adding a known quantity of reagent to the absorbing medium, allowing it to react with the contaminant, and then back-titrating the unreacted reagent with an appropriate standard titrant. In either case, the amount of contaminant is measured by the difference between blank, *B*, and sample, *S*, titers. In the first case, $S-B$ is applicable; in the second, $B-S$. Generally, at 25° C. and 760 mm. of mercury, the following expression applies:

$$\text{P.p.m. by volume} = \frac{\text{titer difference} \times N \times 24.5 \times 1000}{Vc} \quad (5)$$

where N = normality of standard titrant with respect to contaminant

24.5 = liters per equivalent at 25° C. and 760 mm. of mercury

Vc = corrected volume of gas sample, liters

Slide rules may be constructed specifically for solving this equation for parts per million by volume of the individual air contaminant under analysis. The equation is most conveniently rearranged to

$$\frac{Vc}{24.5 \times \text{titer difference}} = \frac{1000 \times N}{\text{p.p.m. by volume}} \quad (6)$$

If two-cycle semilog paper is used, parts per million by volume in the range 1 to 100 and normality of titrant in the range 0.001 to 0.100 N may be plotted on the outside, stationary scales. The normality is plotted as 1000 N, but marked as N—i.e., a N of 0.001 would be plotted as 1000 × 0.001 = 1 but marked on the scale as 0.001. This will satisfy the requirement that individual scales in a scale pair have the same linear unit. Volumes may be plotted in the range 10 to 1000 liters while titer difference (T.D.) is plotted as T.D. × 24.5 but marked as T.D. In this manner, differences in the range 0.4 to 37 ml. may be expressed on the scale. Volumes and titer differences are plotted on the inside, sliding scales.

Slide rules fabricated of cardboard and log paper in this laboratory have an accuracy of within 1%. As most industrial air analyses are performed in the range 1 to 100 p.p.m. by volume with an expected accuracy of ±2 p.p.m. using wet-test meters whose accuracy may be as variant as ±5%, use of this rapid slide rule method for volume corrections and concentration calculations seems justifiable.

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Ascorbic Acid in Analytical Chemistry

Determination of Ferric Ions

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IN ANALYTICAL chemistry ascorbic acid has usually been employed only in an indirect way; the product reduced by it has been determined or the excess of ascorbic acid used in the redox reaction has been estimated iodometrically and the amount consumed by the oxidizing agent found by difference. A method for direct application of ascorbic acid has been developed by Ptitsyn and Kozlov (*5*), who employed freshly prepared ascorbic acid solution for potentiometric determination of ferric(III) ions. The authors have been able to reproduce their results.

Information was received after this work was completed that the reverse procedure has been applied by do Nascimento (*4*), who determined ascorbic acid with ferric chloride.

The great reducing power of ascorbic acid suggested the idea of trying its use as a volumetric solution.

The redox potential of a solution containing ascorbic and dehydroascorbic acids has been compared to a saturated calomel electrode and found to be 0.433 volt at 21° C., which, referred to a normal hydrogen electrode, is equal to +0.185 volt.

This value approaches the numerous but rather divergent data found in the literature (*6*). Ascorbic acid reacts with weak oxidizing materials, producing dehydroascorbic acid. Strong oxidizing reagents, such as potassium permanganate, may also oxidize dehydroascorbic acid. Dehydroascorbic acid is more easily oxidized in alkaline than in acidic medium.

The oxygen of the atmosphere acts catalytically to destroy ascorbic acid, and it is especially affected by traces of heavy metals.

ASCORBIC ACID AS MEASURING SOLUTION

As the gram equivalent of ascorbic acid in the reduction-oxidation process is 88.03, approximately 8.9 grams of ascorbic acid were used for preparing 1 liter of 0.1 N volumetric solution. The water was freshly distilled from a glass apparatus. The normality was checked with 0.1 N iodine solution as well as with 0.1 N potassium iodate solution. When iodine solution was used, 5 ml. of 2 N hydrochloric acid were added to 20 ml. of ascorbic acid solution and the cold solution was titrated without any indicator. In the iodate titration, 1 gram of potassium iodide was added to 20 ml. of 0.1 N potassium iodate, acidified with 5 ml. of 2 N hydrochloric acid, and titrated with ascorbic acid until the yellow color of the iodine disappeared. The use of starch indicator was eliminated, as it decreased the rate of reaction, and a distinct end point may be observed without indicator.

As the values obtained with the two different methods were in good agreement within the limits of experimental error, only potassium iodate was used in further checking; an exact and constant 0.1 N solution is more easily prepared from it.

It may be concluded that the stability of the ascorbic acid solution depends on whether it is kept in an inert atmosphere or in

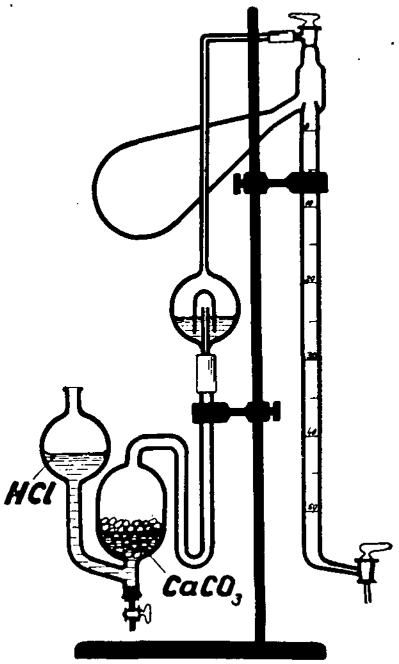

Figure 1

Table I. Changes in Efficiency of 0.1 *N* Ascorbic Acid Solution

Days	1	2	3	4	5	6	7	10	15	20	60
Stored in air											
Factor	0.999	0.996	0.993	0.989	0.984	0.978	0.970	0.960	0.949	0.930	0.717
Diminution, %	...	−0.3	−0.6	−1.0	−1.5	−2.1	−2.9	−3.9	−5.0	−6.9	−28.2
Stored in CO_2											
Factor	0.999	0.996	0.993	0.990	0.990	0.989	0.989	0.989	0.987	0.979	0.943
Diminution, %	...	−0.3	−0.6	−0.9	−0.9	−1.0	−1.0	−1.0	−1.2	−2.0	−5.6

air. The normality of a volumetric solution kept without any particular care showed an average decrease of 0.3 to 0.4% per day during 2 weeks (Table I). This deterioration could not be eliminated by boiling the distilled water, by keeping the solution in a dark bottle, nor by storing it in the cold. Accordingly, if the solution is kept at room temperature in a bottle with a glass stopper, the normality should be checked daily or even twice a day, if it is used frequently.

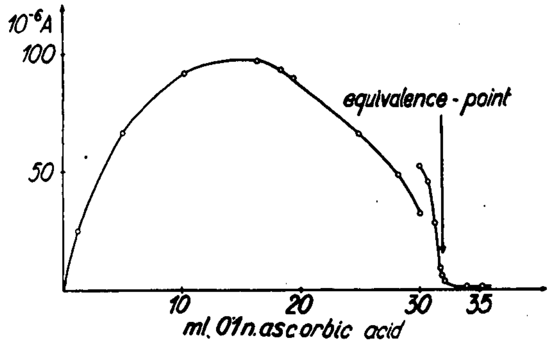

Figure 2

When the volumetric solution was stored in a carbon dioxide atmosphere in a Winkler-type tank buret connected with a carbon dioxide generator (see Figure 1) its normality decreased only in the first 2 days and became constant for 2 weeks thereafter (Table I). This indicates that the deterioration was caused chiefly by atmospheric oxygen.

The change of efficiency depends also upon the quality of the solid ascorbic acid used for preparing the solution.

TITRATION OF FERRIC IONS WITH 0.1 *N* ASCORBIC ACID SOLUTION

The reaction of ferric ions with ascorbic acid is slow at room temperature, especially at the end of the titration. With heating, the rate of reaction increases and the end point can be indicated by potassium sulfocyanate.

$$C_6H_8O_6 + 2Fe^{+++} \rightleftharpoons C_6H_6O_6 + 2Fe^{++} + 2H^+$$

The reproducibility of estimation was first investigated, then compared with other gravimetric and volumetric determinations of ferric ions.

Experiments have been carried out for establishing whether the end point indicated by potassium sulfocyanate changes with temperature. According to the authors' experience, the solution containing ferric ions in slightly acidic medium consumed the same amount of ascorbic acid at 60° C. as in the cold. The same results were obtained if the titration was performed in the reverse direction—i.e., ascorbic acid was determined with ferric ions. Accordingly, the error of the indicator is negligible when 0.1 *N* solutions are titrated in the presence of potassium sulfocyanate.

The dehydroascorbic acid may also react with ferric ions under certain circumstances. This process naturally would interfere with the estimation. To answer this question, a solution was made containing equivalent amounts of dehydroascorbic acid as well as ferrous and ferric ions. The solution was kept for different periods and at various temperatures in neutral and slightly acidic media, and the amount of ferric ion remaining was determined with ascorbic acid in the presence of potassium sulfocyanate. It was established that increase of temperature above 60° C. is not advisable, as at higher temperatures a considerable amount of ferric ion was reduced by dehydroascorbic acid. The acid concentration should be at least 0.1 *N*, as the reducing effect of dehydroascorbic acid is smaller in an acidic medium. At temperatures below 60° C. and in slightly acidic media only a negligible amount of ferric ion was reduced by dehydroascorbic acid during a 5-minute titration.

Experiments were also carried out to establish the effect of the concentration of acid, indicator, and dilution on the end point. No change in end point was noted when the concentration of acid was less than 0.5 *N*. The change of indicator concentration between 0.005 and 0.0005 *N* had no influence on the end point. It was established that highest accuracy could be obtained with ferric ion concentrations between 25 and 250 mg. per 100 ml.

The effect of atmospheric oxygen was studied in parallel tests made in a carbon dioxide atmosphere. It appeared that atmospheric oxygen does not affect the results to any extent. This fact provides a great advantage compared to titanometric (*3*) and chromometric (*7*) determinations of ferric ion.

For establishing the accuracy of the method, comparisons were made with other methods applicable to the determination of ferric ions. The same solution containing ferric chloride in a concentration about 0.1 *N* was analyzed gravimetrically, by the methods of Zimmermann-Reinhardt and Mohr, titanometrically, and by titration with ascorbic acid. The experimental data are presented in Table II. Deviations are smallest in the estimations made with ascorbic acid and the data agree completely with those obtained titanometrically.

To determine the accuracy of the method, the mean error of the averages of twenty parallel assays was determined and found to be 0.004% (Table III).

According to the authors' experience, ferric ions can best be determined as follows:

Table II. Comparison of Methods

(Mg. of Fe per ml.)

	Volumetrical Estimation			
Gravimetric Estimation as Fe_2O_3	With ascorbic acid	Titanometrically (*3*)	According to Zimmermann-Reinhardt	Iodometrically according to Mohr
5.933	5.969	5.964	5.964	6.005
5.975	5.958	5.958	5.952	5.994
5.978	5.964	5.964	5.975	5.977
5.954	5.969	5.969	5.986	5.972
Av. 5.960	5.965	5.964	5.969	5.992

Table III. Accuracy of Method

(29.00 ml. of 0.1 *N* $FeCl_3$ solution titrated with 0.1 *N* ascorbic acid solution)

Ascorbic Acid Solution Consumed, Ml.	
29.00	29.00
29.02	29.01
29.00	29.00
29.00	29.01
28.98	28.98
28.99	28.98
29.03	28.99
29.03	29.01
29.03	29.02
29.02	29.00

Av., 29.00
Mean error, ±0.017
Mean error of average, %, 0.004

The nearly neutral solution containing 25 to 250 mg. of ferric ion should be acidified with 5 ml. of 2 *N* hydrochloric acid in a 250-ml. titration flask, then heated cautiously so that the temperature does not exceed 60° C. Then 1 ml. of 0.5 *N* potassium sulfocyanate is added to the warm solution, which results in a red color. The titration is continued and in the vicinity of the end point the volumetric solution is added drop by drop until discoloration takes place within a few seconds. More than 5 minutes should not elapse between heating and the end of the titration.

One ml. of 0.1 *N* ascorbic acid solution is equivalent to 5.584 mg. of iron, 7.184 mg. of FeO, 7.984 mg. of Fe_2O_3, or 16.221 mg. of $FeCl_3$. The mean error of the average values is ±0.004% in the presence of 25 to 250 mg. of iron.

INFLUENCE OF FOREIGN IONS

Strong oxidizing materials like iodine, iodate, bromate, permanganate, chromate, nitrite, hydrogen peroxide, vanadium (V), cerium(IV), etc., react with ascorbic acid and make the estimation inaccurate. Colorless and difficultly reducible materials do not disturb the titration. Nitric acid in a third molar proportion, and nitrate ions even in multiple molar proportions do not interfere. The reaction is retarded by sulfate and phosphate ions, but even in tenfold molar proportion has no significant influence on the end point. Small amounts of fluoride ions do not interfere with the estimation and only when present in a molar ratio of 1 to 1 did the color of the ferric sulfocyanate fade to such an extent that its change could hardly be observed. In the presence of colored ions potassium sulfocyanate indicator could not be used. In this case the titration may be carried out electrometrically.

DEAD-STOP END-POINT TITRATION

As potassium sulfocyanate can be used only in colorless or slightly colored solutions to indicate the end point, observation of the end point was tried with Foulk and Bawden's (*1*) "dead-stop" method.

The potential of an accumulator was decreased to 0.14 volt through a potentiometer. Two platinum electrodes 2 cm. long and 0.4 mm. in diameter were immersed in the solution to be analyzed and the circuit was closed through the electrodes. The intensity of the current was measured by a microammeter.

Then 0.1 *N* ascorbic acid solution was gradually added to the solution, which was heated to about 60° C. in the vicinity of the end point as in titrations made with potassium sulfocyanate.

The intensity of the current is shown in Figure 2 as a function of the ascorbic acid used. The intensity increased suddenly when the solution was heated, owing to the decrease of internal resistance, then a sharp diminishing could be observed at the equivalence point, after which only the intensity of the residual current could be marked. Accordingly, the end point is indicated by a sharp decrease in intensity. Ions of nickel, cobalt, and chromium do not interfere. The "depolarimetric" estimation was carried out also by the method of Guzman and Rancaño (*2*), when the primary potential was provided by a platinum–platinum-rhodium thermocouple.

ESTIMATION WITH 0.01 *N* ASCORBIC ACID

The estimation of ferric ions can also be performed with 0.01 *N* ascorbic acid. The volumetric solution was freshly prepared on every occasion by dilution of 0.1 *N* ascorbic acid. On the basis of experimental data it can be stated that in the case of 3 mg. of iron the accuracy of the method is satisfactory and is equal to 0.5%. The concentration range 0.1 to 0.5 *N* for hydrochloric acid and 1 ml. of 0.5 *N* potassium sulfocyanate per 100 ml. was found the most suitable.

TECHNICAL POSSIBILITIES OF IRON DETERMINATION WITH ASCORBIC ACID

There is a great advantage for technical analyses in the fact that the determination can be made in a hydrochloric acid medium. Ammonium salts, sulfate and nitric ions, and even small amounts of free nitric acid do not interfere with the end point. An iron salt solution therefore which has undergone the most varied separating operations may be used for the assay without difficulty. The authors have tested among others the iron content of iron ores, sulfide ores, and bauxite, with the aid of this method (Table IV).

Table IV. Determination of Iron

Ore Tested	Ascorbic Acid Method, %	Zimmermann-Reinhardt Method, %
Magnetite	79.87 79.92 79.87	80.60
Pyrite	42.06 42.10 42.06	42.51
Bauxite	21.73 21.71 21.73	21.75

In the case of many technical control tests it has been very difficult to effect the iron determinations in the presence of large amounts of phosphate or fluoride ion. With the present method even small quantities of iron are easily determinable in the presence of large amounts of phosphate and small amounts of fluoride ions.

SUMMARY

Almost all oxidimetric and reductometric methods used previously for determining ferric ions may be replaced by the new ascorbic acid procedure. Over oxidimetric methods it has the great advantage that iron need not be reduced before determination. Ferrous ions can be oxidized by boiling with a few drops of hydrogen peroxide. If nitric acid is present in the solution, it suffices to neutralize it. The method is preferable to the titanometric method, as the volumetric solution is easily prepared, it is much more easily checked, and the influence of atmospheric oxygen is negligible. Compared to the chromometric titration, the preparation of the ascorbic acid reagent does not demand cumbersome procedures, no complicated mechanisms are necessary for its storage, and the estimation in most cases may be carried out without electrometric indication of the end point. In the presence of small amounts of nitric acid and fluoride ions and even large amounts of nitrate and phosphate ions, no interference could be noted.

At present extensive studies are being made of the indirect application of the ascorbic acid determination of ferric ions, as well as of the use of redox indicators. Methods have been developed for the ascorbic acid determination of chlorate, bromate, iodate, and chromate as well as vanadic and ceric ions. Preliminary studies are under way on reductometric determination of other oxidizing materials as well as of organic nitro and nitroso radicals by this new procedure.

A colorimetric method has recently been developed, which is based on the strong change of color caused by ascorbic acid. The reactions between ascorbic acid and molybdic acid and tungstic acid, respectively, have been applied for establishing traces of metals catalytically. The results will be published shortly.

The name "ascorbinometry" is proposed for this method.

ACKNOWLEDGMENT

The authors are indebted to Éva Bányai, Mrs. L. Buzás, Zsuzsanna Faber, and György Rády for their valuable assistance.

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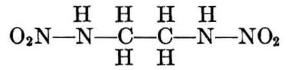
Received December 1, 1950.

CRYSTALLOGRAPHIC DATA

53. Ethylenedinitramine (Haleite, Edna)

Contributed by W. C. McCRONE, Armour Research Foundation, Illinois Institute of Technology, Chicago 16, Ill.



$$\begin{array}{c} \mathrm{H}\quad\mathrm{H}\quad\mathrm{H}\quad\mathrm{H} \\ O_2N-N-C-C-N-NO_2 \\ \mathrm{H}\quad\mathrm{H} \end{array}$$

Structural Formula for Ethylenedinitramine

EXCELLENT crystals of ethylenedinitramine can be obtained by recrystallization from water, dioxane, ethyl alcohol, nitromethane, acetone, or acetic acid. The habit varies from massive to plates depending upon the solvent used. A hemimorphic rod habit is obtained on recrystallization from water in which the wetting agent Stearonyx is dissolved. This habit shows the forms right bisphenoid {111} and {110}. As ordinarily obtained from water or dioxane, ethylenedinitramine recrystallizes as a massive habit having forms {001}, {111}, and {110} (Figure 1). Figure 4 is an orthographic projection of this habit from water. When recrystallized from ethyl alcohol, a habit is obtained which shows only the bipyramid form {111}. Recrystallization from nitromethane or acetone gives plate habits with forms {001}, {100}, {010}, and {111} or {010}, {100}, and {111}, respectively.

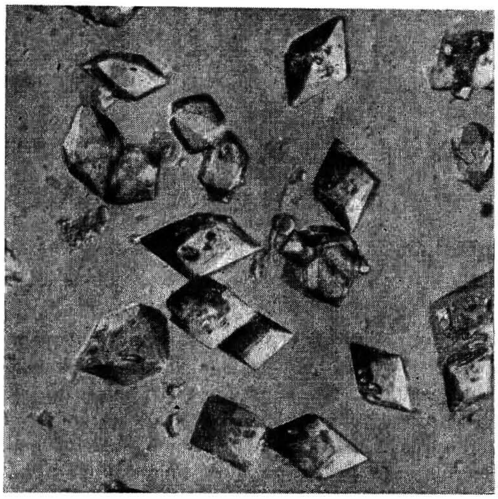


Figure 1. Crystals of Ethylenedinitramine from Water

Figure 2. Ethylenedinitramine Sublimate

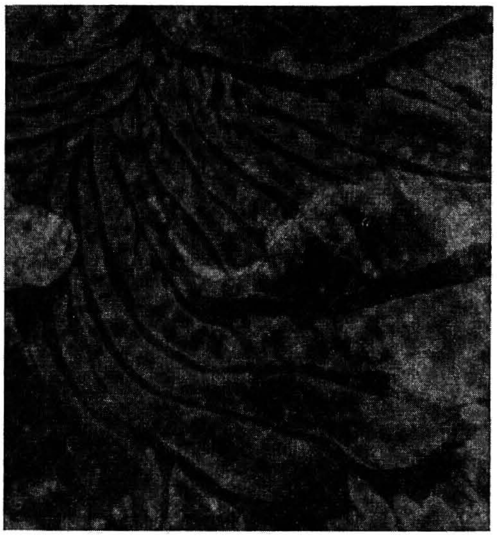


Figure 3. Ethylenedinitramine from Fusion

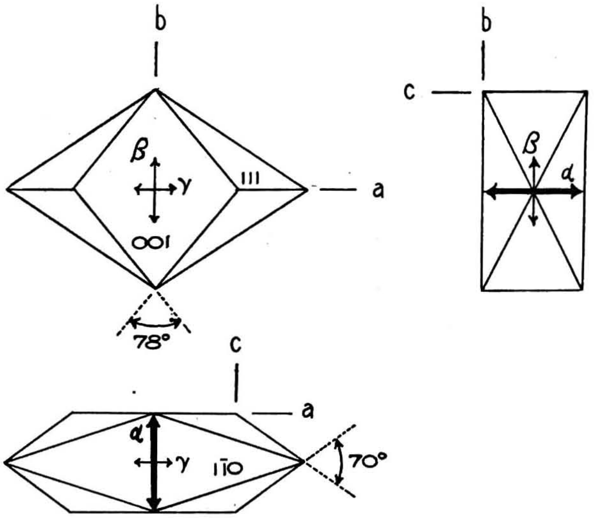


Figure 4. Orthographic Projection of Typical Crystal of Ethylenedinitramine from Water

CRYSTAL MORPHOLOGY
Crystal System. Orthorhombic.
Form and Habit. Massive, rods, or plates showing bipyramids, {111}, prisms, {110}, basal pinacoid, {001}, and occasionally the pinacoids {100} and {010}.
Axial Ratio. $a:b:c = 0.812:1:0.571$.
Interfacial Angles (Polar). $110 \wedge 1\bar{1}0 = 102°$.
X-RAY DIFFRACTION DATA
Cell Dimensions. $a = 8.80$; $b = 10.84$; $c = 6.19$.

Formula Weights per Cell. 4.
Formula Weight. 150.1.
Density. 1.73 (flotation); 1.70 (x-ray).

Principal Lines

d	I/I_1	d	I/I_1
5.4	0.80	2.36	0.06
4.55	0.83	2.28	0.06
3.67	0.16	2.25	0.11
3.40	1.00	2.18	0.06
3.08	0.60	2.12	0.20
2.97	0.44	2.02	0.06
2.70	0.06	1.975	0.02
2.66	0.27	1.870	0.02
2.56	0.44	1.830	0.10
2.52	0.20	1.790	0.10

OPTICAL PROPERTIES

Refractive Indexes. (5893 A.; 25° C.). $\alpha = 1.427 \pm 0.002$. $\beta = 1.686 \pm 0.002$. $\gamma = 1.73 \pm 0.005$.

Optical Axial Angles. (5893 A.; 25° C.). $2V = (-)44°$. $2E = 78°$.

Dispersion. $v > r$, slight; dispersion of birefringence, very strong.

Optic Axial Plane. 010.

Acute Bisectrix. $\alpha = c$.

Extinction. Parallel and symmetrical.

Molecular Refraction (R) (5893 A.; 25° C.). $\sqrt[3]{\alpha\beta\gamma} = 1.609$. R(calcd.) = 31.3 (using $k = 9.94$ for N_2O_2). R(obsd.) = 30.0 (assuming $d = 1.73$).

FUSION DATA. Ethylenedinitramine sublimes when heated to give easily recognized dendrites, well-formed skeletal plates and tablets (Figure 2). The plates are usually six-sided lying on 001, show indexes β and γ, and give a centered BX_a figure. The optic axial angle, $2E$, is 78°. Ethylenedinitramine melts at 178–179° C. with considerable decomposition. It solidifies spontaneously to give a characteristic terrace pattern of gas bubbles (Figure 3). The crystals show few markings, no measurable angles, and very anomalous polarization colors. A mixed fusion with thymol gives feathery dendrites, showing α parallel to the direction of growth and γ in the other direction. The index α is less than the index of thymol melt, while the index γ is greater than that of the melt.

ACKNOWLEDGMENT

Most of the work described was carried out on a contract between Cornell University and the Office of Scientific Research and Development during June 1943 to July 1944. It was described in OSRD Report No. 3014 recently declassified by the Ordnance Department of the Army. Acknowledgment is due to Alfred T. Blomquist, who was technical representative of OSRD Section B-2-A during the progress of this work, and to Colonel H. M. Roberts of the Ordnance Department for his efforts in regrading this report. John H. Andreen and Sien-Moo Tsang were also associated with this project and contributed to the above description. Acknowledgment is also due to Frederic V. Schossberger, who assisted in the determination of the powder x-ray diffraction data, and to John Krc, who assembled these data for publication.

CONTRIBUTIONS of crystallographic data for this section should be sent to Walter C. McCrone, supervisor, Analytical Section, Armour Research Foundation of the Illinois Institute of Technology, Chicago 16, Ill.

SCIENTIFIC COMMUNICATION

Chromatographic Behavior of Difructofuranoses

THE application of paper chromatography to the analysis of sugar mixtures is dependent upon similar analysis of pure sugars. In the course of work on polyfructosans we have had occasion to develop such chromatographs of the three difructofuranoses (difructose anhydrides I, II, and III). It is of interest that the difructofuranoses travel at a more rapid rate than does fructose when a butanol-pyridine-water 3:2:1 mixture is used at 20° C. as the developing agent. A comparison of the migration distances of the five difructose anhydrides compared to that of fructose is as follows:

Fructose	1
Difructose anhydride I	1.14
Difructose anhydride II	1.30
Difructose anhydride III	1.72
Diheterolevulosan[a] I	0.34
Diheterolevulosan[a] II	0.70

[a] Similar chromatographs of the diheterolevuloses have been reported by H. C. S. deWhalley, N. Albon, and D. Gross in collaboration with F. W. Zerban and L. Sattler in their work on nonfermentables of cane molasses as well as acid and heat degradation products of fructose [*Analyst*, 76, 287 (1951)].

As it has been generally found that the distance traveled by a sugar decreases with increase in molecular size, this behavior of the difructofuranoses is of particular interest. Researches on these sugars and their relations to the polyfructosans are now in progress and the results will be published at a later date.

EMMA J. McDONALD
BETTY K. GOSS

National Bureau of Standards
Washington, D. C.

RECEIVED December 18, 1951

Book Review

Practical Electron Microscopy. *V. E. Cosslett.* xi + 299 pages. Academic Press, Inc., 125 East 23rd St., New York 10, N. Y., 1951. Price, $5.50.

Workers entering the field of electron microscopy and many whose experience is on an operational level have long needed a volume that has both an adequate presentation of the physics of the electron microscopy and a critical evaluation of the techniques and applications that have so far been developed. Cosslett has accomplished this task most successfully. The physics of the electron microscope is treated thoroughly and the presentation at an intermediate level should be understandable to anyone familiar with introductory college physics. The approach in the chapters on specimen techniques is very welcome, for here is a critical discussion that will help workers evaluate the available methods of specimens preparation in the chemical and metallurgical fields as well as the biological, and, most important, indicates the applicability and limitations involved.

This reviewer has some minor points of disagreement—e.g., the value of unshadowed plastic replicas, the alignment procedure suggested, or emphasis on European models. More important is the lack of guidance for the uninitiated in his first reading. Minor revisions in certain chapters with a note in the preface would provide an excellent introduction to the subject. After some experience with the instrument, a careful and thorough reading should be very rewarding. BENJAMIN M. SIEGEL

NEW BOOKS

The Lemon Fruit. Its Composition, Physiology, and Products. *Elbert T. Bartholomew* and *Walton B. Sinclair.* xi + 162 pages. University of California Press, Berkeley 4, Calif. $4.50.

Typical Microstructures of Cast Iron. *The British Cast Iron Research Association,* Alvechurch, Birmingham, England. 53 pages. £1. 1s. 0d.

Chicago Chemical Conference

THE All-Day Chemical Conference of the Chicago Section, AMERICAN CHEMICAL SOCIETY, was held in Chicago November 25, 1951. Abstracts of the papers presented before the Inorganic and Analytical Section are given here.

New Method for Calculating pH Limits at the End Point of a Titration. W. P. CORTELYOU, Roosevelt College of Chicago, Chicago, Ill.

New, simple mathematical formulas have been developed for calculating the pH when a solution of an acid, base, or salt has been 99.9% titrated and when it has been 100.1% titrated, or between any other such limits. This provides a considerable improvement in the solution of the problems of indicator selection and feasibility of titration.

Rapid Test for the Detection of Groundwood. R. HUBATA, Armour and Co., Chicago, Ill.

A new and rapid test for the detection of groundwood (lignocellulose) in paper and other products of wood was described. When aqueous biiodate is applied to paper which contains groundwood, a deep brown stain immediately develops. The same results are obtained by using iodate in dilute mineral acid solution. Experiments were made in order to explain the reaction that takes place.

Dielectric Indicator for Column Chromatography. DONALD E. LASKOWSKI AND RICHARD E. PUTSCHER, Armour Research Foundation, Chicago, Ill.

Many methods have been used to detect the presence of colorless compounds during the course of a chromatographic separation. The refractive index of the effluent has been widely used by many investigators. Various color-forming streak reagents have also been used. Arbitrary fractionation of the effluent and examination of the solute has been used successfully in a large number of separations. It is sometimes possible to detect colorless compounds by their ultraviolet fluorescence.

Troitskiĭ [*Biokhimiya*, 5, 375 (1940)] described a device that measured the dielectric constant of the material adsorbed on a chromatographic column. Although the method of Troitskiĭ worked, it was felt that a device that would continuously measure the dielectric constant of the eluate would better serve as an indicator for detecting colorless compounds.

The work described in this paper is an evaluation of such an instrument. Various cell designs were described and their performances were shown. The use of this instrument in several practical chromatographic separations was described. The instrument used is commercially available and can be used without modification to give excellent results.

Several New Methods of Analysis with a Rotating Mercury Electrode. T. S. LEE, University of Chicago, Chicago, Ill.

The electrode consists of about 0.1 ml. of mercury in a round Bakelite cup that is rotated at 200 to 1800 r.p.m. Electroreducible and electro-oxidizable substances in aqueous solution yield current-voltage curves (waves) similar to those obtained from the dropping mercury electrode. The height of the wave is proportional to concentration and can be used to determine, with an accuracy of about 1 to 2%, electroreducible substances at concentrations as low as 5×10^{-7} *M*—e.g., 0.06 p.p.m. of cadmium ion. Theoretical equations for the shape of the wave have been derived and verified.

A coulometric method has been devised for the determination of metal ions at concentrations as low as 7×10^{-9} *M*—e.g., 0.8 part per billion of cadmium. A constant reducing potential is applied to the rotating electrode for 15 minutes. During that time some of the metal ion is reduced and accumulates in the mercury. A less reducing potential is then applied and the amount of electricity that corresponds to the redissolution of the metal is measured. From this quantity the concentration can be calculated with an accuracy of 1 to 5%.

Similar methods can be used to analyze mixtures of metal ions that have half-wave potentials differing by as little as 30 mv. This is made possible by the proper selection of the potentials applied for accumulation and dissolution.

The first and higher derivatives of the current-voltage wave can be obtained by suitable electrical circuits as described by O. Müller. The derivative curves are useful in the analysis of mixtures, as mixtures that would yield overlapping current-voltage waves give derivative curves consisting of separated peaks.

Selection of Solvents in the Ultraviolet Spectrophotometric Determination of Phenols. WALTER MAHLER AND J. ROY DOTY, Bureau of Chemistry, American Dental Association, Chicago, Ill.

In water or alcohol solutions (polar solvents) the phenols all show a broad absorption band in the region between 2700 and 3000 A. The bands are too similar to permit identification of a particular phenol and overlap to too great an extent to permit the determination of one phenol in the presence of another.

In a nonpolar solvent such as iso-octane the band is generally resolved into two principal peaks, with decrease in band width (Brode, W. R., "Chemical Spectroscopy," p. 205, 2nd ed., New York, John Wiley & Sons, 1943). The ultraviolet absorption curves become sufficiently characteristic to allow the quantitative determination of isomers of substituted phenols.

The application of this principle to the determination of phenolic compounds in therapeutic products was described.

Ion Exchange Equilibria Involving Fission Products and Thorium in Uranyl Nitrate. JACK SCHUBERT, Argonne National Laboratory, Chicago, Ill.

The reactions between a synthetic cation exchange resin and many of the fission products and thorium in uranyl nitrate have been studied under the following conditions: varying concentration of uranyl nitrate, carrier-free levels of fission products and thorium; and concentration of fission products and thorium varied by addition of carriers, constant uranyl nitrate concentration.

A simple mass active formulation describes the results with fair accuracy, except in cases where radiocolloid formation occurs.

Determination of Hydroperoxides in Petroleum Products. D. C. WALKER, Standard Oil Co. (Indiana), Whiting, Ind.

An arsenometric method was presented for the determination of hydroperoxides in petroleum products. The method utilizes a two-phase extraction and reduction of the hydroperoxides with alkaline sodium arsenite. Excess arsenite is determined iodometrically. Known concentrations of hydroperoxides in gasoline, heater oil, white oil, and wax were determined quantitatively with a reproducibility of ±0.01 peroxide numbers less than 1; for peroxide numbers above 1, the reproducibility is within 1%. Results are independent of sample size, which ranges from 10 to 100 ml., depending upon the hydroperoxide content.

Means for Increasing Sensitivity of the Beckman DU Spectrophotometer. H. M. GRUBB AND L. J. SCHMAUCH, Standard Oil Co. (Indiana), Whiting, Ind.

Changes in the amplifier and null circuit which increase the sensitivity of the photometer by a factor of 10 or more were described.

This is accomplished without loss of photometering accuracy by adding an extra stage of amplification. Use of subminiature tubes in the final two stage allows this to be done in the existing amplifier compartment. An extra 15-volt battery required may be housed elsewhere.

Analysis by Differential Electrical Migration in Polyphase Systems. HAROLD H. STRAIN, T. R. SATO, AND W. P. NORRIS, Argonne National Laboratory, Chicago, Ill.

The differential migration of solutes produced by flow of solvent in a polyphase system forms the basis of the widely applicable chromatographic adsorption analysis. Analogous separations are now being made in polyphase systems when electrical current produces the migration of ionized or charged solutes. This differential electrolysis is carried out conveniently in media such as moist paper, gels, and beds of porous filter aids, ion exchangers, etc. The separability of some mixtures may be increased by electrolysis in one direction in one solvent followed by transverse migration in another solvent. Separations may be made continuously by the flow of solvent transversely to the simultaneous flow of electrical current. In all these applications of differential electrical migration, the effect of the electrode reactions and the separability of the mixtures depend primarily upon the solvent, the electrolytic solution. These migration methods have been applied to the separation of mixtures of various organic and inorganic substances such as organic acids and inorganic anions and cations. Separations may be made qualitatively or quantitatively. The migration behavior of many ions indicates the formation of unexpected complex substances in the solutions.

Automatic Coulometric Titrations with Externally Generated Reagents. Applications to Iodometry. James N. Pitts, E. A. Schmall, and Donald D. DeFord, Northwestern University, Evanston, Ill.

An automatic instrument for the performance of coulometric titrations with externally generated reagents has been employed successfully for the titration of arsenic(III) with electrolytically generated iodine. The use of a new type, single-arm, generation cell, and a curent of 100 ma. gives precisions and accuracies of the order of ±0.2% on samples in the range from 0.15 to 0.6 me.

5,7-Dihydroxy-4-methylcoumarin as a Fluorescent Indicator. Harold Podall, Edwal Laboratories, Inc., Ringwood, Ill.

5,7-Dihydroxy-4-methylcoumarin has been found to exhibit interesting fluorescent properties in dilute aqueous solution. If the pH of an acid solution of the compound is gradually increased by the addition of a base, a sharp and intense increase in fluorescence occurs. The change occurs in the pH range of 5.5 to 5.8 and is reversible. Under ultraviolet irradiation the fluorescence is intense enough to be observed in daylight.

This change in fluorescence with a change in the pH of the solution has suggested the possible use of this coumarin as a fluorescent indicator in acid-base titrimetry. Trial of the compound with the use of 0.01 N and 0.1 N acids and bases gives precision of 0.3% or better in observation of the end points. End points are more easily observed than in similar titrations with phenolphthalein. The coumarin can be used in concentrations of 10^{-4} to 10^{-2}%, the more dilute solutions giving sharper changes in fluorescence.

5,7-Dihydroxy-4-methylcoumarin may be especially useful in acid-base titrations of murky, colored, or very dilute solutions. It is a good substitute for *p*-nitrophenol as an indicator.

Other fluorescent indicators were also discussed.

Coordination Number of the Nickelous Ion. Leonard I. Katzin, Argonne National Laboratory, Chicago, Ill.

It is known that cobaltous ion can show two coordination numbers, 6 and 4. The latter is found with moderately strong complexing agents, and with solutions of the halide or thiocyanate salts in organic solutions. The higher coordination number is characteristic of aqueous solutions, organic solutions of the nitrate, etc. Nickel forms both hexahydrated salts and complexes with four groups attached, and a transition between the two coordination numbers should be demonstrable. This is found on comparing the complexes of the ion with the several halide ions, in organic solution. Spectrophotometric investigation shows the complexes with the iodide ion retain the higher coordination number in large part, while the chloro complexes and thiocyanate complexes have the lower coordination number. This indicates the drop in coordination number to be somewhat more difficult than for cobaltous ion.

Interactions of Divalent Cations with Substituted Ethylenediamines. R. Kent Murmann and Fred Basolo, Northwestern University, Evanston, Ill.

The formation and complexity constants have been measured at 0° and 25° C. for copper(II) and nickel(II) complexes with ethylenediamine, and *N*-methyl, *N*-ethyl, *N*-isopropyl, and *N,N'*-diethylethylenediamine in 0.5 M potassium nitrate–water solution. The method of Bjerrum was used, appropriately modified to suit present requirements. In addition, the thermodynamic quantities $\Delta H°$, $\Delta F°$, and $\Delta S°$ have been evaluated for each reaction in the stepwise formation.

Since the basicities of the amines are nearly equal, steric hinderance was expected to exert a large influence on the formation constants. The magnitude of this steric effect was the present concern. Both the formation and complexity constants indicated that the steric effect overshadowed the much smaller base strength effect. Nickel(II) complexes, having a coordination number of 4 and 6, tetrahedral and octahedral configurations, respectively, exhibit greater steric hindrance to their formation than does copper(II), which has a coordination number of 4 and a planar configuration. The difference is not so great as might be anticipated from a consideration of molecular models.

Relation of Electronic Density to Chemical Combination. R. T. Sanderson, State University of Iowa, Iowa City, Iowa.

The chemical inactivity of atoms of the inert elements is considered to be related not only to their particular number and distribution of electrons, but also to the particular average density (ED) of their electronic atmosphere. A "stability ratio (SR)" is defined as the ratio of the average density of an atom or ion to that of an isoelectronic (real or hypothetical) inert element atom. Unit SR thus represents maximum stability. SR values are a measure of relative electronegativities of both atoms and simple ions. This paper discussed the application of SR values toward explaining many common chemical phenomena, including the bond "shortening" usually ascribed to resonance among single covalent and ionic or multiple covalent bond structures, and the chemical reactivity of atoms and their ions.

Silyl and Silylmethylamines as Bases. The Double Bond Character of the Silicon-Nitrogen Bond. Sei Sujishi and Samuel Witz, Illinois Institute of Technology, Chicago, Ill.

It is generally assumed that the silyl group has a greater +I effect than the methyl group. However, it is found that trisilylamine is a much weaker base than trimethylamine (Burg). This has been attributed to the stabilization of the trisilylamine by resonance of the electron pair on the nitrogen atom with the vacant L-orbital in the silicon atom.

In order to observe whether the silyl group has any tendency to increase the base strength, it was of interest to study the base strengths of the series of amines in which methyl groups are systematically replaced by silyl groups.

For this purpose dimethylsilylamine and methyldisilylamine were synthesized. Dimethylsilylamine has not been previously isolated. In comparison to the other silylamines, dimethylsilylamine has some unusual properties.

Trimethylamine is known to form a reaction stable addition compound with trimethylboron (Brown and Taylor). Dimethylsilylamine has been found to combine with trimethylboron, but this compound is much more dissociated than the trimethylamine compound. Methyldisilylamine has been found not to combine with trimethylboron, even at −112° C. A. Burg has previously reported that trisilylamine does not combine with trimethylboron.

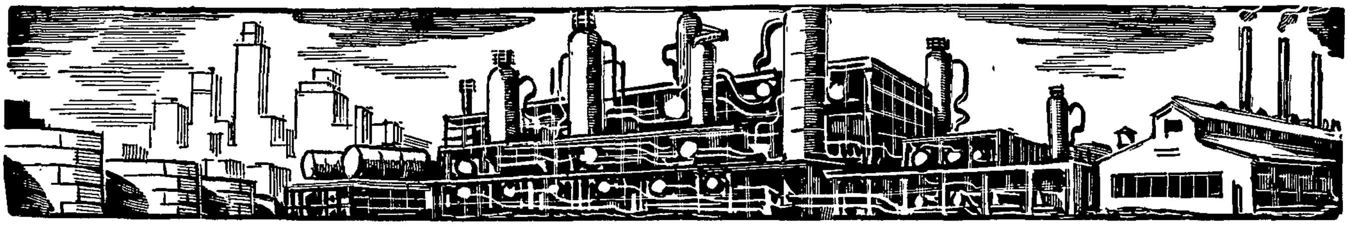
Hence, with trimethylboron as reference acid, replacement of even one methyl group in trimethylamine leads to a considerable decrease in the basic property. This supports the interpretation that resonance effects mask any inductive (+I) effect that the silyl group may possess.

The reactions of the silylamines with boron trifluoride and hydrogen bromide have also been studied. The results lead to the same conclusion as do the experiments with trimethylboron.

Self-Diffusion in Solid Sodium. N. H. Nachtrieb, J. A. Weil, E. Catalano, and A. W. Lawson, Institutef or the Study of Metals, University of Chicago, Chicago, Ill.

Measurements were reported for the self-diffusion of solid sodium at 1 atmosphere pressure over the temperature range 0° to 95° C. The data fit the empirical equation $D = 0.320 \exp(-10{,}650/RT)$ with an uncertainty of ±300 cal. mole^{-1} in the heat of activation. The entropy of activation calculated from the temperature coefficient of the elastic modulus is 7.7 E.U., and is in good agreement with the value based upon the vacancy mechanism.

Measurements of the diffusion rate at high hydrostatic pressures were interpreted in terms of the vacancy model for diffusion. A correlation was found between the diffusion coefficient and the melting point of sodium as a function of pressure. It was shown that for sodium and a number of other cubic metals the heat of activation for self-diffusion is proportional to the latent heat of fusion.



Symposium on Modern Methods of Analytical Chemistry

THE fifth annual Louisiana State University Symposium on Modern Methods of Analytical Chemistry was held in Baton Rouge, La., Jan. 28 to 31. Abstracts of the papers are given below. Inquiries regarding publication of papers presented at the symposium should be addressed to the individual authors.

Instrumentation. R. H. MÜLLER, Los Alamos Scientific Laboratory (four lectures), Los Alamos, N. M.

General instrumental developments, transducers, new primary elements, *n-p-n* junction transistors. New phenomena and methods of potential interest to the analyst.

Precision coulometric integrators, wide-range recording differential refractometry, automatic determination of micro melting points, and thermistor methods for microdeterminations of molecular weight.

Instrumental approaches to chromatography and ion exchange.

Recording, computing, data assimilation, and interpretation.

Coulometric Titrations with Externally Generated Reagents. DONALD D. DEFORD, Northwestern University, Evanston, Ill.

The external generation technique of performing coulometric titrations involves generation of the desired reagent by electrolysis of a suitable electrolyte solution in a separate generator cell. This reagent is then delivered to the vessel which contains the sample, where the titration reaction occurs. The technique is, therefore, very similar to an ordinary titration which employs a standard solution of the reagent. However, instead of being determined by a measurement of the volume of standard solution, the quantity of reagent used is determined by a measurement of the coulombs of electricity required to produce it.

Various designs of generator cells for producing reagents were described and the results of typical titrations employing these reagents were presented.

The external generation technique offers several distinct advantages over the internal generation technique in certain analyses:

Extraneous ions in the sample do not interfere with the generation of the reagent. For example, hydroxyl ion cannot be titrated by anodically generated hydrogen ion in the presence of chloride if the internal generation technique is employed. As chloride is more easily oxidized than water, the desired anode reaction, two molecules of water yielding four protons, four electrons, and one molecule of oxygen, does not proceed with 100% current efficiency. If the hydrogen ion is generated at the anode of a separate generator cell, employing sodium sulfate as the electrolyte, this difficulty is not encountered.

One can adjust the composition and concentration of the generator electrolyte and of the sample solution independently, so that optimum conditions for both the generation and the titration can be achieved.

The electrical field that exists between the generator electrodes is isolated from the sample solution and thus does not interfere with any of the conventional electrometric methods for locating the end point of the titration reaction.

The external generation technique also possesses certain disadvantages and limitations:

There is a small but finite time between generation of the reagent and delivery of the reagent to the sample solution. This delay necessitates small blank corrections in some titrations.

Impurities in the generator electrolyte may interfere. In the internal generation technique such interfering impurities can usually be titrated before the sample is introduced, and thus they cause no error. Pretitration of impurities is not generally feasible with the external generation technique.

The volume change which must necessarily occur when externally generated reagents are delivered to the sample solution often prevents application of this technique to small sample volumes.

Generally speaking, the external generation technique appears to be most applicable to "macro" titrations (roughly 0.1 to 5 me. of sample contained in a volume of about 25 to 250 ml.). The technique is very well suited to automatic titrations of several types of samples. Some automatic titrators were described and the results obtained with these instruments in typical titrations were presented. Some preliminary results in the field of automatic continuous titration of samples in flow streams were also discussed.

Application of Radio-Frequencies to Chemical Analysis. OLEN A. NANCE, Louisiana State University, Baton Rouge, La.

DIELECTRIC AND CONDUCTIVITY MEASUREMENTS. The classical methods of measurement were reviewed critically from the standpoint of general principles and applicability to devices employing electrodes isolated from the system being measured. Sources of data were also discussed, together with the limitations to be expected in connection with lack of uniformity as to frequency and other experimental factors. Some attention was given to the status of theoretical treatments as they affect analysis.

DESIGN FACTORS. The electronics and analytical requirements for satisfactory development in this field were discussed. Particular stress was placed on the development of routine analytical models, the possibilities of the instrument for control, and some of the possible future developments in this field. Because cell design represents the major unsolved problem, particular attention was given to analyzing the cell requirements for various applications.

COMMERCIALLY AVAILABLE INSTRUMENTS. A brief critique of currently available instruments was undertaken with representatives of interested manufacturers contributing to a general discussion. Several instruments were on display.

REFERENCE DATA COLLECTION. The prediction of future applications of this technique requires the accumulation of data not now available in the literature. Some of the most pressing questions were reviewed and the value of additional data was illustrated. Stress was also placed on precautions necessary to ensure that the information obtained is presented in standard terms and upon some of the confusion inherent in both classical and current reports.

APPLICATIONS AND LIMITATIONS OF HIGH FREQUENCY INSTRUMENTS. Group discussion of present and future applications with particular emphasis on the study of electrolytes, nonelectrolytes, and systems involving precipitation or the determination of solids content.

Inorganic Microchemistry. PHILIP W. WEST, Louisiana State University, Baton Rouge, La.

THE SCOPE AND PHILOSOPHY OF MICROCHEMISTRY. Historical. Current status and trends.

MICROCHEMICAL SEPARATIONS. Volatilization, precipitation and gathering, chromatography, extraction, complexation, and electrochemical.

IDENTIFICATION METHODS. Microscopical. Ordinary light and polarized light.

Spot tests. Classification and significance of reaction types.

Special methods. Fluorometric methods, spectroscopical, x-ray, etc.

QUANTITATIVE METHODS. "Classical" approaches, bioassay methods, optical methods, and electrical methods.

Activation Analysis. M. T. KELLEY, Oak Ridge National Laboratory, Oak Ridge, Tenn.

DEFINITION AND PRINCIPLES OF ACTIVATION ANALYSIS. Nuclear reactions. Fundamental equations of activation.

SENSITIVITY AND APPLICABILITY OF ACTIVATION

ANALYSES WITHOUT CHEMICAL SEPARATION. Analysis by direct radiation measurement. Analysis by means of physical characteristics of radiation emitted.

ANALYSES INVOLVING CHEMICAL SEPARATIONS. Separations without carrier. Separation with added carriers.

APPLICATIONS OF NEUTRON ACTIVATION ANALYSIS.

Organic Analytical Reagents. FRANK WELCHER, University of Indiana, Bloomington, Ind.

The application of analytical methods to an increasingly large number of materials, and attempts to detect and determine smaller quantities of substances in these materials, have created many problems. To eliminate interference, develop more sensitive methods, and discover simpler procedures, many new analytical reagents have been studied. Because of their number and variety, organic compounds have proved most useful. Among these compounds are found reagents for all common analytical functions: solvents, wash liquids, acids, bases, oxidants, reductants, and complex forming compounds. Because of their numbers, an empirical search among the existing organic compounds for analytical reagents is virtually impossible. Furthermore, because of the possibility of synthesis, many substances that may prove useful as reagents have not yet been prepared. Consequently, the search must extend to all possible compounds as well as to existing ones. Obviously, such an investigation will be facilitated by a knowledge of the relation of the structure of the molecule and its analytical function.

The most important group of organic analytical reagents consists of compounds capable of forming chelate compounds with metal ions.

Certain groups are necessary for the formation of these important analytical substances. Among these are —OH, —CO_2H, =NOH, —CO—, and —NH_2. The 5- and 6-membered rings found in chelate compounds are possible only when the acidic and/or coordinating groups necessary for their formation are properly located in the molecule with respect to one another. With these principles clearly understood, the search for new reagents is greatly simplified.

Interference is a major problem of the analytical chemist. One of the desirable objectives in the application of organic compounds in chemical analysis is the development of specific or highly selective procedures. Certain atomic groupings confer the property of specificity or selectivity on organic molecules. For example, the α-dioximes yield red precipitates with nickel salts, and the α-acyloin oximes form insoluble green copper salts. Finally, both sensitivity and selectivity may be improved by an understanding of weight and volume effects, steric consideration, and by a knowledge of the solubilizing influence of certain atomic groupings.

Coulometric Titrations. W. D. Cooke, Cornell University, Ithaca, N. Y.

A discussion of the historical aspects of coulometric analysis, principles of electrolytic oxidation and reduction, various types of procedures, and the advantages and disadvantages as compared to conventional procedures, instrumentation, and problems in continuous analysis.

High precision coulometric titrations, the present status and some problems in analyses at extreme dilution, an electrometric approach to millimicrogram and micromicrogram samples, and some new end-point techniques and their applications.

Quantitative Organic Analysis Via Functional Groups. Sidney Siggia, General Aniline and Film Co., Easton, Pa.

Applicability of this type of analysis to the needs of the organic analyst.

Fundamental principles involved in choosing reactions to be used for the analyses and how these principles are applied.

Problems that can arise when using a certain reaction and how these problems are overcome or circumvented. Reaction completeness, equilibrium, solvent and titration problems (discussion of nonaqueous titrations). Interferences. Avoiding separation of components.

Separating components (distillation, extraction, precipitation, dialysis, electrodialysis, chromatographic adsorption, electrophoresis).

Identification techniques using quantitative functional group analysis.

Radioactivity Analysis. S. A. Reynolds, Oak Ridge National Laboratory, Oak Ridge, Tenn.

Definition and Scope. Determination of the quantity of radioactivity present, also, in many cases, the nuclide(s) responsible for the activity (qualitatively or quantitatively).

Instrumental Methods of Analysis. Measurement of radioactivity. Alpha: proportional counter. Beta: Geiger-Müller, proportional, and 100%-geometry counters. Gamma: G-M and proportional counters, ionization chambers, and scintillation counters.

Decay Studies. Resolution of decay curves. Special instruments.

Energy Measurements. Absorption techniques. Beta-ray spectrometry. Scintillation spectrometry. Alpha measurements. X-ray measurements.

Separation Techniques. Separations without "carrier." Solvent extraction, distillation, electrodeposition, ion exchange.

Separations with added carrier. Isotopic and nonisotopic carriers. Qualitative analysis: scheme, nucleonic aids. Quantitative analysis: yield correction, advantages, difficulties (scattering, etc.).

Applications. Radioisotope assay. Methods for common radioisotopes. Accuracy.

Fission-product methods. Philosophy. Examples.

Tracers in analytical chemistry. Application of above principles in use of radioactive tracers in conventional analytical chemistry.

Separation and Analysis of Sugars and Related Compounds by Ion Exchange Chromatography. L. P. Zill, Oak Ridge National Laboratory, Oak Ridge, Tenn.

Analytical usefulness of a method for the separation and analysis of sugars and related compounds.

Previous observations on the formation of ionic complexes of sugars by reaction with borate ions.

Application of ion exchange chromatography to the separation of borate-sugar complexes.

Quantitative analysis of the separated sugars.

Analysis of synthetic and natural sugar mixtures.

Extension of the method to other polyhydroxy compounds such as the sugar alcohols, glycosides, nucleotides, etc.

Future studies and applications of the method.

Micromethods for Characterization of Organic Compounds. Nicholas D. Cheronis, Brooklyn College, Brooklyn, N. Y.

The classical approach in dealing with an unknown organic compound involves: (1) purification and determination of the purity of the unknown; (2) systematic study to ascertain whether the compound in question does or does not bear complete similarity in physical and chemical properties to one of the large number of organic substances described in the chemical literature; (3) determination of the structure and classification if the compound under study is not known.

Micromethods were discussed in detail:

The concepts of "absolute" and "operational" purity.

Criteria used in the establishment of purity: solubility, melting point, boiling point, optical properties, distribution between immiscible solvents.

Problems involved in proof of identity. Rigorous proof based upon similarity of physical and chemical properties and upon similarity of one or two properties.

The traditional approach for establishing whether an unknown solid consists substantially of one component or two or more is simplified by the introduction of optical methods. Among the simpler ones is the microscopical examination of melting and crystallization phenomena, by which it is possible to determine rapidly: crystal habit, formation of eutectic, melting temperature, and refractive index of the melt.

Micromethods for the preliminary examination of liquids.

Determination of melting points. A critical discussion of all methods used for the determination of capillary and micro melting points. The need for better methods of frequent restandardization of thermometers. The confusion of the "melting points of organic compounds." The effect of strains in the crystal lattice.

Steps used in various schemes of systematic characterization.

Classification of the unknown based upon: solubility and elements present; ionization constants and elements present.

Further restriction of classification of unknown by means of "functional group tests." Selection of tests and problems involved in application and limitation of the tests. Brief discussion of some new tests: chromatographic (paper) and use of tetrazolium salts for detection of reducing groups.

Coordination of data and deduction of probable identity.

Final proof of identity by derivization. Discussion of factors involved in the selection of derivatives. Critical discussion of effect of the purity of derivitizing agent; ratio of reactants; effect of preparative and purification procedures; problems involved in coordinating observable melting point data with values listed in the literature.

Simplification of the systematic approach by the experienced worker. Illustration of short cuts in the identification of organic compounds in very small amounts of samples: analysis of 2 drops of liquid used for doping of race horses; identification of the active component in a beauty finger nail preparation; identification of the active components in a remedy used for athlete's foot.

Correction

In the book "Reagent Chemicals, American Chemical Society Specifications, 1950" on page 41 under the heading "Substances darkened by hot sulfuric acid" the third line was repeated as the fifth line. The fifth line should read: "(in a brine bath) for 30 minutes, keeping the test tube covered with a."

THE ANALYST'S CALENDAR. . .

Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy

THE Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, sponsored by the Analytical Chemistry Group, Pittsburgh Section, AMERICAN CHEMICAL SOCIETY, and the Spectroscopy Society of Pittsburgh, will be held at the Hotel William Penn, Pittsburgh, Pa., March 5 to 7, 1952. An exposition of modern laboratory equipment will be a part of the conference. A.S.T.M. spectroscopy meetings will also be held. While not a part of the conference, conferees are welcome to attend.

At 8:30 A.M., March 5, registration will begin in the Fort Duquesne Room, Hotel William Penn, and the exposition will open in the Fort Duquesne and Urban rooms.

The following preliminary program has been arranged:

Wednesday Morning, March 5

OPENING SESSION

HUGH F. BEEGHLY, Presiding

9:30 **Welcome.** C. BURTON CLARK, Chairman, Spectroscopy Society of Pittsburgh.
J. K. MILLER, President, Analytical Chemistry Group, Pittsburgh Section, ACS.

9:40 **Pittsburgh's Analytical Chemists Serve the World.** J. C. WARNER, President, Carnegie Institute of Technology.

10:00 **Pellet Method Using Silver Powder for Spectrochemical Analysis of Low-Alloy Steel.** ERNEST H. S. VAN SOMEREN, Editor, *Spectrochimica Acta.*

10:50 **Role of the Analyst in Industrial Hygiene.** DUDLEY A. IRWIN, Medical Director, Aluminum Co. of America.

Wednesday Afternoon

ANALYTICAL CHEMISTRY

C. MANNING DAVIS, Presiding

2:00 **Polarographic Studies with Solid Electrodes.** L. B. ROGERS AND SAMUEL S. LORD, JR., Massachusetts Institute of Technology.

2:35 **High Frequency Measurements in Chemical Analysis.** PHILIP J. ELVING, Pennsylvania State College and Harvard University.

3:10 **Polarographic Determination of Lead in Beryllium.** RALPH W. BANE, Argonne National Laboratory.

4:00 **Application of Polarographic Methods to Analysis of Materials Encountered in Zinc Smelting Operations.** PHOEBE RUTHERFORD, LOUIS A. CHA, AND JACK A. MEREDITH, St. Joseph Lead Co. of Pennsylvania.

4:25 **Determination of Tungsten in Titanium Metal.** E. W. BEITER, Westinghouse Research Laboratories.

4:40 **Solvent Extraction in Steel Analysis. Conditions for Removal of Iron(III) as the Thiocyanate Complex.** LABEN MELNICK AND HENRY FREISER, University of Pittsburgh, AND HUGH F. BEEGHLY, Jones and Laughlin Steel Corp.

5:00 **Statistical Study of the Reliability of Analytical Methods as Applied in Practice in an Industrial Research Laboratory.** O. D. SHREVE AND H. B. WAGNER, E. I. du Pont de Nemours & Co., Inc.

SPECTROISOTOPY

MARY E. WARGA, Presiding

2:00 **Spectroisotopy, a New Field of Spectroscopic Endeavor.** J. R. MCNALLY, JR., Oak Ridge National Laboratory.

2:35 **Use of Discharge Tubes in Spectrochemical Analysis.** MARK FRED, Argonne National Laboratory.

3:10 **Applications of Photoelectric Recording of Spectra to the Study of Electrical Discharges of Gases.** T. M. DONAHUE, Johns Hopkins University.

4:10 **Radioisotopes and Solvent Extraction.** GEORGE H. MORRISON, Sylvania Electric Products, Inc.

4:40 **Determination of Small Concentrations of Indium by Radioactivation.** J. E. HUDGENS AND L. N. NELSON, U. S. Atomic Energy Commission.

MASS SPECTROMETRY

A. G. SHARKEY, JR., Presiding

2:00 **Recent Developments in Mass Spectrometry.** ALFRED O. NIER, University of Minnesota.

2:30 **Appearance Potential and Ionization Probability by Monoenergetic Electrons.** R. E. FOX, W. M. HICKAM, T. KJELDAAS, AND D. GROVE, Westinghouse Research Laboratories.

2:50 **High Frequency Ion Resonance Mass Spectrometer.** G. JERNAKOFF, General Electric Co.

3:10 **Dual-Purpose Mass Spectrometer.** A. P. GIFFORD, SYBIL M. ROCK, AND P. S. GOODWIN, Consolidated Engineering Corp.

4:00 **Mass Spectrometer-Digital Computer Combination for Automatic Analysis.** W. S. YOUNG, J. H. RAMSER, R. A. BROWN, F. W. MELPOLDER, G. R. CARRICK, J. SPONTAK, AND C. E. HEADINGTON, Atlantic Refining Co.

4:30 **Automatic Conversion of Mass Spectra to Digital Form.** SYBIL M. ROCK, CLIFFORD E. BERRY, AND R. L. SINK, Consolidated Engineering Corp.

Wednesday Evening

GEORGE KELCH, Presiding

8:00 **Scientific Solution of Mysteries.** JOSEPH D. NICOL, Director, Pittsburgh and Allegheny County Crime Laboratory.

8:40 Social Hour. In the tradition of the Snack Sessions which have done so much to promote fellowship and informal discussion at the meetings of both the Spectroscopy Society and the ACS in Pittsburgh, the Social Hour will provide an opportunity to relax and get acquainted. The exposition is in adjoining rooms and will remain open until 10:00 P.M. Refreshments and a light snack will be served. All conferees are invited to attend as the guests of the cooperating societies.

Thursday Morning, March 6

EMISSION SPECTROSCOPY

C. BURTON CLARK, Presiding

9:00 **Some Fundamental Aspects of Spectrochemical Processes Encountered in Determining Major Constituents.** LESTER W. STROCK, Strock Laboratories, Inc.

9:20 **Effect of Changing Conditions of the Light Source upon the Influence of Extraneous Materials in Spectrochemical Analysis.** D. Andrychuk and C. McMullen, Diamond Alkali Co.

9:35 **Analysis of Photographic Emulsion Calibration Using a Step Sector.** J. Sherman and M. Slavin, Philadelphia Naval Shipyard.

10:05 **GE Sun Lamp for Emulsion Calibration.** A. J. Mitteldorf, Armour Research Foundation of Illinois Institute of Technology.

11:00 **Internal Standard Properties of Undispersed-Selective Filtered Radiation.** J. H. Enns, University of Michigan.

11:20 **Effect of Argon and Argon-Helium Mixtures on the Direct Current Arc.** S. James Adelstein and Bert L. Vallee, Massachusetts Institute of Technology.

11:40 **Determinations of Trace Elements by Combining Chemical Enrichment and Spectrochemical Methods.** G. E. Heggen, Albany Medical College, and L. W. Strock, Saratoga Springs Commission.

12:00 **Spectroscopic Determination of Metals in Silica-Alumina Cracking Catalysts.** J. P. Pagliassotti and F. W. Porsche, Standard Oil Co. of Indiana.

ANALYTICAL CHEMISTRY

A. H. Bushey, Presiding

9:00 **Oligo- or Trace Elements in Biology.** Bert L. Vallee, Massachusetts Institute of Technology.

9:40 **Electrochemical Method for Oxygen Determination in Gases.** M. G. Jacobson, Mine Safety Appliances Co.

10:00 **Application of Molybdenum-Catalyzed Reductions to Determination of Molybdenum, Chlorate and/or Perchlorate, Nitrate and/or Nitrite, and Possibly Other Irreversibly Reduced Oxy Ions or Oxygen-Containing Materials Such as Nitro-Organic Compounds.** G. P. Haight, Jr., and Alan Reynard, George Washington University.

10:20 **Universal Combustion System.** A. N. Oemler and J. Mitchell, Jr., E. I. du Pont de Nemours & Co., Inc.

11:00 **Determination of Arsenic in Canned Fruits.** J. C. Bartlet, Ethel List, Margaret Wood, and R. A. Chapman, Food and Drug Laboratories, Department of National Health and Welfare, Canada.

11:20 **Alkalimetric Determination of Phosphate after Separation of Calcium by Ion Exchange.** B. H. Kindt, E. W. Balis, and H. A. Liebhafsky, General Electric Co.

11:40 **2-(*o*-Hydroxyphenyl)-benzoxazole as a Reagent for the Determination of Cadmium.** Joseph L. Walter and Henry Freiser, University of Pittsburgh.

12:00 **Two Rapid Methods for Determination of Metallic Ions in Gum Arabic.** William H. Martin, Harris-Seybold Co.

MASS SPECTROMETRY

W. S. Young, Presiding

9:00 **Extension of Mass Spectrometer Analysis to Various Nonhydrocarbon Molecules.** Fred L. Mohler, National Bureau of Standards.

9:20 **Mass Spectra of Heterocyclic Nitrogen Compounds.** G. S. Cook and A. P. Marr, Laramie Laboratories, U. S. Bureau of Mines.

9:40 **Mass Spectra of the Tetramethyl Compounds of Carbon, Silicon, Germanium, Tin, and Lead.** V. H. Dibeler, National Bureau of Standards.

10:00 **Determination of Benzene, Cyclohexane, and Methylcyclopentane in Light Naphthas by Mass Spectrometer.** Seymour Meyerson, Standard Oil Co. of Indiana.

10:50 **Benzene, Toluene, Xylene, Ethylbenzene, Cumene, and Total C_9 Aromatics.** J. H. Shively and J. J. Morello, The Texas Co.

11:10 **Mass Spectrometric Method of Resolving Normal and Isomeric Paraffins in Complex Hydrocarbon Mixtures.** H. Sobcov, Socony-Vacuum Laboratories.

11:30 **Correlation of Mass Spectra of Alcohols through C_{11}.** R. A. Friedel and A. G. Sharkey, Jr., Bureau of Mines.

ULTRAVIOLET SPECTROPHOTOMETRY

R. A. Friedel, Presiding

9:00 **A Decade of Ultraviolet Absorption Spectroscopy.** E. J. Rosenbaum, Sun Oil Co.

9:30 **Iodobenzene and Its Derivatives as Examples of Abnormal Chromophoric Interaction in the Benzene Series.** L. Doub and J. M. Vandenbelt, Parke, Davis & Co.

9:50 **Some Potentialities of the 200- to 230-Millimicron Range in Biochemical Studies.** Leo J. Saidel, Chicago Medical School.

10:15 **Use of Micrometer Baly Cells with Beckman and Cary Ultraviolet Spectrophotometers.** R. C. Hirt and F. T. King, American Cyanamid Co.

10:50 **Spectrophotometric Practice with Absorption Cells of Extremely Short Path Length.** J. M. Vandenbelt, Carola Henrich, and Shirley L. Bash, Parke, Davis & Co.

11:00 **Ultraviolet Absorption Analysis for C_9 and C_{10} Aromatics.** Matthew S. Norris and Norman D. Coggeshall, Gulf Research and Development Co.

11:20 **Ultraviolet Spectrophotometric Study of Eugenol-Isoeugenol System.** V. C. Vespe and D. F. Boltz, Wayne University.

11:35 **Ultraviolet Absorption Studies of Factors Affecting the Fading of Humic Acid Solutions.** Harold L. Lovell and Corliss R. Kinney, Pennsylvania State College.

Thursday Afternoon

ANALYTICAL CHEMISTRY

J. F. Miller, Presiding

2:00 **Titrations in Nonaqueous Solutions.** Ernest G. Wollish and Charles W. Pifer, Hoffmann-La Roche, Inc.

2:50 **Anodic Voltammetry of Phenol.** John F. Hedenburg and Henry Freiser, University of Pittsburgh.

3:10 **Comparison of Analytical Behavior of the Chelates of 2-(*o*-Hydroxyphenyl)-benzothiazole and 2-(*o*-Hydroxyphenyl)-benzothiazoline.** Robert G. Charles and Henry Freiser, University of Pittsburgh.

4:00 **Relation of Structure to Analytical Behavior of Some Substituted 8-Hydroxyquinolines.** W. Dwight Johnston and Henry Freiser, University of Pittsburgh.

4:20 **Effects of Solvents upon the Potentiometric and Visual Titration of Organic Acids, Bases, and Salts in Nonaqueous Medium.** Charles W. Pifer, Morton Schmall, and Ernest G. Wollish, Hoffmann-La Roche, Inc.

4:45 **New Technique for Extraction and Titration of Salts of Organic Bases and Acids.** Morton Schmall, Charles W. Pifer, and Ernest G. Wollish, Hoffmann-La Roche, Inc.

5:05 **Determination of β-Propiolactone Purity.** Willard P. Tyler and Donald W. Beesing, B. F. Goodrich Research Center.

5:20 **Quality of Water Produced by Ion Exchange.** A. C. Reents and J. F. Wantz, Illinois Water Treatment Co.

ULTRAVIOLET, INFRARED, AND MASS SPECTROMETRY

Foil A. Miller, Presiding

2:00 **Use of Variable Reference Spectrophotometry in Qualitative Analysis.** J. H. Jones and L. S. Harrow, U. S. Food and Drug Administration.

2:30 **Use of the Beckman DU Spectrophotometer in the Region from 1 to 2 Microns.** Locke White, Jr., Walter B. Wade, and Willis Woodruff, Jr., Southern Research Institute.

2:45 **Study of Application of Matrices and IBM Techniques to the Analysis of Liquid Hydrocarbon Mixtures by Mass Spectrometry.** H. Sobcov, Socony-Vacuum Laboratories.

INDEXING AND ABSTRACTING SPECTROMETRIC DATA

Foil A. Miller, Presiding

3:25 **Report on Cooperative Abstracting of Infrared Articles.** Thomas V. Parke, Eli Lilly and Co.

3:45 **Present Status of the NRC Punch Card Project.** E. Carroll Creitz, National Bureau of Standards.

4:05 **Keysort File of Mass Spectra for Qualitative Analysis.** Sybil M. Rock, Consolidated Engineering Corp.

4:25 **Proposal for Cooperative Abstracting of Ultraviolet Articles.** Thomas V. Parke, Eli Lilly and Co.

4:45 **Indexing and Sorting of Infrared, Ultraviolet, Mass, and Other Standard Data on IBM Equipment.** L. E. Kuentzel, Wyandotte Chemicals Corp.

Friday Morning, March 7

EMISSION SPECTROSCOPY

Julia Senko, Presiding

9:00 **Direct-Reading Analysis of Steel-Making Slags.** M. F. Hasler and F. Barley, Jr., Applied Research Laboratories.

9:30 **Effect of Entrance Optics of the Direct-Reading Spectrometer upon the Analysis of Stainless Steels.** J. J. Jurmain, G. Wright, and S. H. Walters, Baird Associates, Inc.

10:00 **Spectrochemical Determination of Minor Constituents of Stainless Steel.** Charles H. Corliss and Bourdon F. Scribner, National Bureau of Standards.

10:15 **Spectrographic Determination of Sodium and Potassium in Coal Ashes.** C. H. Anderson and C. D. Beatty, Babcock & Wilcox Co.

10:50 **Efficacy of Low Inductance AC Spark Techniques for Aluminum Alloys.** J. T. Rozsa and L. E. Zeeb, National Spectrographic Laboratories.

11:10 **Routine Spectrographic Analysis of Impurities in Electrolytic Copper.** Ray E. Wright, Utah Copper Division, Kennecott Copper Corp.

11:30 **Routine Spectrographic Analysis of Impurities in Anode Copper.** Ray E. Wright, Utah Copper Division, Kennecott Copper Corp.

12:00 **Conversion of an ARL High-Voltage Spark Source to Air-Interrupted Operation.** Fred Holzer, James H. Herron Co.

RAMAN AND INFRARED SPECTROMETRY

J. J. McGovern, Presiding

9:00 **Design and Performance of the Perkin-Elmer Model 99 Double Pass Monochromator.** C. D. Cowles, Perkin-Elmer Corp.

9:20 **Improvements in Infrared Spectroscopy.** W. A. Patterson, Baird Associates, Inc.

9:55 **Analytical Applications of the Raman Quantometer.** M. F. Hasler, J. W. Kemp, and G. Andermann, Applied Research Laboratories.

10:50 **Rotation-Vibration Spectra of Allene and Allene-d_4.** R. C. Lord and P. Venkateswarlu, Massachusetts Institute of Technology.

11:10 **Infrared Spectral Differentiation between Paraffinic, Cyclopentyl, and Cyclohexyl Structural Groups.** S. A. Francis, The Texas Co.

11:30 **Olefin Group-Type Analysis by Infrared Absorption.** Eleanor L. Saier, Abbott Posefsky, and Norman D. Coggeshall, Gulf Research and Development Co.

11:55 **More about Olefin Group Correlations in the Infrared.** James D. Stroupe, Rohm & Haas Co.

MASS SPECTROMETRY

R. E. Fox, Presiding

9:00 **Geochemistry of the Stable Carbon Isotopes.** H. B. Craig, University of Chicago Institute for Nuclear Studies.

9:20 **Variation of O^{18}/O^{16} Ratios in Calcium Carbonate of Marine Shells and Their Implications.** S. Epstein and H. A. Lowenston, University of Chicago Institute for Nuclear Studies.

9:40 **Mass Spectrometer Study of Silicon Tetrafluoride.** Robert E. Rummel, John R. Sites, and Russell Baldock, Oak Ridge National Laboratory.

10:00 **Mass Spectrometer Investigation of UF_3.** L. O. Gilpatrick, Russell Baldock, and John R. Sites, Oak Ridge National Laboratory.

10:40 **Mass Spectrometer Study of Technetium.** Russell Baldock, John R. Sites, and L. O. Gilpatrick, Oak Ridge National Laboratory.

11:00 **Needle-Valve Type of Variable Gas Leak.** E. F. Babelay and L. A. Smith, Carbide and Carbon Chemicals Co.

11:20 **Automatic Level Controller and Distributing Mechanism for Liquid Nitrogen.** P. Rochlin, R. M. Gutter, and J. V. R. Kaufman, Ordnance Corps, Picatinny Arsenal.

USE OF X-RAY TECHNIQUES IN ANALYTICAL CHEMISTRY

Harold P. Klug, Presiding

9:00 **Combined X-Ray Absorption and Diffraction Technique for Quartz Analysis.** Jean Leroux and Don Lennox, Industrial Health Laboratory, Department of National Health and Welfare, Canada.

9:25 **X-Ray Diffraction Method for Analysis of Bauxite Exploration Samples.** R. H. Black, Aluminium Laboratories, Ltd.

10:45 **X-Ray Diffraction Method for Determining the Origin of Industrial Dusts.** Lawrence L. Schmelzer, California Department of Public Health.

11:20 **Analysis of High Temperature Alloys by X-Ray Fluorescence.** R. M. Brissey, General Electric Co.

11:50 **Quantitative Analysis with the Fluorescent X-Ray Spectrograph.** Howard F. Carl, U. S. Bureau of Mines.

Friday Afternoon

SPECTROPHOTOMETRIC METHODS OF CHEMICAL ANALYSIS

2:00 **Spectrophotometric Adaptation of the Zirconium-Alizarin Sulfonate Method for Fluorides.** E. A. Arnold and M. A. Levitin, Case Institute of Technology.

2:20 **Spectrophotometric Method for the Determination of Fluorides.** H. E. Bumsted and J. C. Wells, Indiana State Board of Health.

2:35 **Ultraviolet Spectrophotometric Determination of Cobalt.** G. Telep and D. F. Boltz, Wayne University.

3:15 **Spectrophotometric Determination of Iron with Sulfuric Acid.** Robert Bastian, Richard Weberling, and Frank Palilla, Sylvania Electric Products, Inc.

3:40 **Spectrophotometric Method for Following Dichromate Oxidations.** M. J. Cardone and J. W. Compton, Wyandotte Chemicals Corp.

4:05 **Spectrophotometric Determination of Titanium.** Edward Hines and D. F. Boltz, Wayne University.

4:25 **Nephelometric Determination of NO_2 and Nitrite.** W. H. Hill and T. F. Hatch, University of Pittsburgh.

4:45 **Absorptometric Method for Determination of Rutin in Buckwheat Leaf Meal and Other Plant Materials.** Arthur Turner, Jr., Eastern Regional Research Laboratory.

EMISSION SPECTROSCOPY

E. S. Hodge, Presiding

2:00 **Analytical Applications of Fluorescent Spectra of Aqueous Solutions of the Rare Earths.** V. A. Fassel, R. H. Heidel, and F. Huke, Institute for Atomic Research and Department of Chemistry, Iowa State College.

2:20 **Conducting Briquet Technique of Spectrographic Analysis. Analysis of Zirconium Metal as the Oxide.** V. A. Fassel, A. M. Howard, and D. O. Anderson, Institute for Atomic Research and Department of Chemistry, Iowa State College.

2:40 **Spectrochemical Analysis of Zirconium Oxide.** E. J. Spitzer and D. D. Smith, Oak Ridge National Laboratory.

3:00 **Quantitative Spectrochemical Analysis of Rare Earth Mixtures.** J. A. Norris and C. E. Pepper, Oak Ridge National Laboratory.

3:40 **Spectrochemical Analysis of Beryllium in Biological Tissue.** Janus Y. Ellenburg and Louis E. Owen, NEPA Project, Oak Ridge.

4:00 **Spectrographic Method for Copper in Beer.** John J. Stansbrey and Rosalind M. Dean, Anheuser-Busch, Inc.

4:20 **Precision of the First Phase of Preparation of Limestone Samples.** R. K. Leininger and Robert F. Blakely, Indiana Department of Conservation, Geological Survey.

4:40 **Precision of Final Preparation of Limestone Samples.** Robert F. Blakely and R. K. Leininger, Indiana Department of Conservation, Geological Survey.

5:00 **Determination of Xenon in Krypton.** J. Allen Wheat and Roy L. Williams, Air Reduction Co.

INFRARED SPECTROMETRY

Norman D. Coggeshall, Presiding

2:00 **Determination of the Mineral Constituents of Rocks by Infrared Spectroscopy.** J. M. Hunt and D. S. Turner, Carter Oil Co.

2:25 **Infrared Spectra of Evaporated Films.** J. E. Tyler and S. A. Ehrhardt, Interchemical Corp.

2:45 **A Horizontal Cell and Its Application to Kinetic Studies by Infrared Spectroscopy.** H. Hausdorff and Vincent J. Coates, Perkin-Elmer Corp.

3:05 **Quantitative Infrared Analysis of Mixtures of Solids by Suspension in Nonpolar Solvents.** Meyer Dolinsky, Food and Drug Administration.

3:55 **Infrared Spectrophotometric Study of Veratrum Alkaloids.** Gilles Papineau-Couture and R. A. Burley, Ayerst, McKenna, and Harrison, Ltd.

4:10 **Infrared Absorption of Ethyl Iodophenylundecylate and Some Related Compounds.** Don H. Anderson, Eastman Kodak Co.

4:35 **Rapid and Highly Accurate Method for the Analysis of Synthesis Gas.** G. L. Barthauer and A. Haggerty, Pittsburgh Consolidation Coal Co.

4:55 **Interferometric Method of Determining the Resolution of an Infrared Spectrometer.** Vincent J. Coates and H. Hausdorff, Perkin-Elmer Corp.

A.S.T.M. COMMITTEE MEETINGS

Committee D-2 on Petroleum Products and Lubricants, Research Division IV on the Hydrocarbon Analysis, Section F. Spectroscopic Methods for the Analysis of Hydrocarbons. Tuesday Evening, 7:00 P.M. W. S. Young, Chairman

Committee E-13 on Absorption Spectroscopy. Wednesday Afternoon, 4:30 P.M. W. R. Brode, Chairman

Committee E-2 on Emission Spectroscopy. Thursday Afternoon, 2:00 P.M. B. F. Scribner, Chairman

The conference dinner will be held on Thursday, March 6, at 6:30 P.M. in the ballroom of the Hotel William Penn. The speaker will be Henry S. Frank, head of the Department of Chemistry, University of Pittsburgh. H. V. Churchill will act as toastmaster. Tickets, $5 each, are available at the registration desk before 1 P.M., Thursday.

Metropolitan Microchemical Society

The Seventh Annual Symposium of the Metropolitan Microchemical Society, on the theme of "Instrumental Methods of Analysis," is to be held February 29 and March 1 at Fordham University, New York.

February 29

8:15 P.M. **Welcome.** N. S. Kuettel, chairman, Metropolitan Microchemical Society.

8:20 **From Gadgets to Instruments in Microchemistry.** H. K. Alber.

9:20 **Inorganic Fluorometric Analysis.** C. E. White.

March 1

10:00 A.M. **Ultraviolet Photometric Titrations.** C. E. Bricker.

11:00 **Infrared Absorption.** R. C. Gore.

2:00 P.M. **Quantitative Ultramicrochemistry in Clinical Laboratories.** A. E. Sobel.

3:00 **An Ultrafine High Precision Microburet.** R. Gilmont.

The Symposium Committee is composed of A. Mistretta, Heyden Chemical Co., Princeton, N. J., and E. Hoffmann and William Rinehart, Interchemical Corp., New York, N. Y. The meeting will be preceded by a mixer and dinner on Friday evening.

Fifth Annual Summer Symposium on Analytical Chemistry

The Fifth Annual Summer Symposium sponsored by the Division of Analytical Chemistry of the American Chemical Society and Analytical Chemistry will be held Friday and Saturday, June 20 and 21, 1952, on the Michigan State College campus at East Lansing, Mich.

The theme of the meeting will be "Analysis of Materials for Ingredients of Unknown Constitution." The topic is designed to treat problems that are daily occurrences in every analytical laboratory. Contributions have been invited critically presenting a number of techniques which may help to identify, characterize, and differentiate as well as determine the constituents of the sample, such as spectroscopy, x-ray and electron diffraction, activation analysis, etc. A number of case histories are being planned which will illustrate the analytical approach to such problems in areas as diverse as air pollution, metals, plastics and resins, and biochemistry.

Headquarters for the symposium will be the Kellogg Center for Continuing Education which has outstanding facilities for conferences, including an auditorium, dining facilities, and accommodations for registrants and families. A ladies' program is being planned.

The chairman of the symposium is R. P. Chapman, Analytical and Testing Division, American Cyanamid Co. The committee on local arrangements is under the chairmanship of Elmer Leininger, Department of Chemistry, Michigan State College.

Philadelphia Analytical Group

The March meeting of the Analytical and Microchemical Group of the Philadelphia Section, American Chemical Society, will be held March 6 at 8:15 P.M. at the Philadelphia Museum School of Art. James J. Lingane, associate professor of chemistry at Harvard University, will speak on "Current Aspects of Polarography," in an informal lecture providing discussion of questions and problems presented by the audience.

Sixth Annual Symposium on Modern Methods of Analytical Chemistry. Louisiana State University, Baton Rouge, La., February 2 to 6, 1953

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

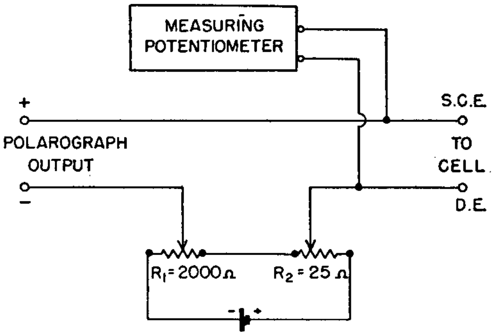
International Congress on Analytical Chemistry. Oxford, England, September 4 to 9, 1952

AIDS FOR THE ANALYST . . . . .

Wave Spreader for Precision Determination of Half-Wave Potential with the Sargent Model XII Polarograph.

David N. Hume and Theodore W. Gilbert, Massachusetts Institute of Technology, Cambridge 39, Mass.

The precision with which half-wave potentials may be measured with automatically recording polarographic apparatus is often limited by the amount that the wave can be "spread out" on the recording paper. The Sargent Model XII is provided with an adjustment by which the voltage drop across the slide-wire may be varied between 3 volts and less than 100 mv. If the wave may be recorded with a low span voltage—e.g., 0.2 volt—it becomes sufficiently spread out to allow the half-wave potential to be determined with considerable precision. The authors have found the simple wave-spreading device shown in the figure to be of great value with this instrument, in that it allows polarograms to be taken with a low span voltage, even though the voltage range of interest may be in the region of 1 to 2 volts.



The device consists essentially of two wire-wound potential dividers of the type used in radio receiver construction, and a source of voltage such as a 1.5-volt dry cell. By adjustment of R_1 (coarse) and R_2 (fine), a voltage is introduced into the circuit just great enough to bring the potential of the dropping electrode to a point about 0.1 volt before the beginning of the wave to be examined. The span voltage of the polarograph is then set at a convenient value—e.g., 0.2 to 0.4 volt. An auxiliary potentiometer is used to measure accurately the potential of the dropping electrode against the working anode at the beginning and at the end of the polarogram, and the calibration points marked on the photographic record by opening the shutter briefly at each point. If desired, R_1 and R_2 may be adjusted to set the potential of the dropping electrode at some exact starting potential, as measured with the potentiometer—e.g., −1.5000 volts. Using a "students'" type potentiometer and a small lamp and scale galvanometer, the initial and final potentials of the polarogram can be measured to ±0.1 mv. without difficulty, although the resultant standardization of the voltage scale on the photographic record is probably not better than ±2 mv.

The polarogram is recorded, the residual and diffusion currents are determined, and the apparent half-wave potential is read by an interpolation between the calibration points. If there is appreciable iR drop through the cell, this should be determined and applied as a correction to give the true half-wave potential. For reversible reactions, the same values of half-wave potential are obtained regardless of whether average or maximum galvanometer swings are used; the latter are considerably more convenient if the galvanometer swing is appreciable. With the unsymmetrical waves often obtained in irreversible electrode reactions, half-wave potentials obtained by different methods of measurement may not coincide exactly. This, together with the fact that the half-wave potential of an irreversible wave is not applicable in the usual polarographic equations, should be recognized by everyone working with such systems.

A series of seven determinations of the half-wave potential of cadmium in 2 M potassium nitrate at 30° C. using a 0.2-volt span gave a maximum deviation of 1.8 mv. and an average deviation of 1.1 mv. by this method. The mean value, −0.5786, compares favorably with two measurements, −0.5765 and −0.5767, made on the same system with the manual apparatus of Lingane and Kolthoff [*J. Am. Chem. Soc.*, **61**, 825 (1939)]. The major source of error in the automatic recording apparatus appears to be in the calibration and measurement of the photographic record. The highest reproducibility which might reasonably be expected for polarograms recorded on the 0 to 2 volt scale is ±10 mv.

A great increase in both accuracy and convenience is obtained if the wave spreader is used when an analysis of the wave is to be made. With a 0.2-volt span, eight or ten points may be taken on the rising part of the wave for plotting values of $\log[i/(i_d - i)]$ against E. Analysis of the cadmium waves in 2 M potassium nitrate gave uniformly straight lines with very little scatter of points and slopes within 5% of the theoretical. Although the wave spreader was designed for use with the Sargent Model XII polarograph, it is equally applicable to any other type of automatic recording polarographic apparatus, the span voltage of which can be varied between 0 and 0.4 volt.

Thermostated H-Cell for Polarography.

Joseph C. Komyathy, Francis Malloy, and Philip J. Elving, The Pennsylvania State College, State College, Pa.

While the H-type polarographic cell first suggested by Lingane and Laitinen [Lingane, J. J., and Laitinen, H. A., Ind. Eng. Chem., Anal. Ed., 11, 504 (1939)] has found wide application due to its simplicity and versatility, no provision was made for maintaining the sample solution at constant temperature, as is usually necessary, except by immersion of the cell in a constant temperature bath, which is somewhat inconvenient. For simplicity of operation, a water jacket was sealed around the sample leg of the cell, permitting water at a constant temperature to be circulated around the sample [Elving, P. J., and Teitelbaum, C., *J. Am. Chem. Soc.*, **71**, 3916 (1949)]. Subsequently, it was felt that provision should also be made for controlling the temperature of the calomel electrode in the other leg of the H-cell. Because of the variation in temperature in the laboratory throughout the day and night, the potential of the saturated calomel reference electrode was not constant. Any variation in the electrode potential of the saturated calomel electrode would cause an error in the measurement of the half-wave potential. In addition to thermostating the entire H-cell, it was desired to modify the cell so as to avoid certain difficulties encountered in the use of an H-cell for polarography. The cell finally designed is shown in Figure 1.

The H-cell is sealed into a large glass tube, so that the cross arm of the H is at a slight angle to the horizontal; the lower end of the cross arm is joined to the sample leg of the H-cell, thus facilitating drainage of solution from the cross arm when the cell is emptied. The ends of the large glass tube are closed and fitted with connections for circulating water. A thermometer well, E, is sealed into the water jacket to allow ready monitoring of the temperature of the cell.

The reference electrode leg of the H-cell was modified by necking down the bottom of the leg in order to prevent the calomel used in the cell from coming in contact with the platinum wire dipping into the mercury. The internal diameter of the leg at the narrowest point is such that the clearance between the glass tube containing the platinum wire and the electrode leg is 1 mm. In preparing the saturated calomel electrode, mercury is added until the level is above the constricted part of the leg (level *B*); this level was selected to give the maximum area of contact between the calomel and mercury. The glass tube containing the platinum wire is placed in the mercury, calomel is added to level *C*, a layer of potassium chloride crystals is placed above the calomel, and the leg is filled to level *D* with saturated potassium chloride solution. The electrode leg is closed with a stopper containing a hole of such diameter that the stopper slides easily over the glass tube containing the platinum wire; a split stopper can conveniently be used.

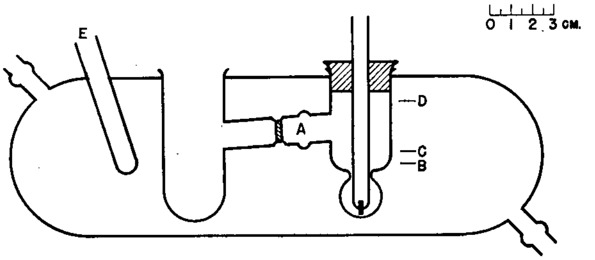


Figure 1

With continued use of the conventional H-cell, the agar plug has a tendency to become loose, permitting solution to seep in between the plug and the fritted glass disk or forming an open space between the plug and disk. Such behavior may result in an abnormal increase in the resistance of the cell or contamination of sample and reference electrode solutions. In order to overcome this difficulty, the diameter of the arm containing the agar plug, *A*, was enlarged slightly at its mid-point. When the agar is placed in the arm, a ridge is formed due to the enlarged diameter, which keeps the agar plug in place.

A stand for holding the cell is made by boring a hole of diameter equal to the external diameter of the water jacket in a block of wood and cutting the block in half along the long axis. Three rubber bands 0.25 inch (0.6 cm.) wide placed around the water jacket at convenient points serve to cushion the cell in the block.

Several such cells have been in operation for the past year.

ACKNOWLEDGMENT

The authors wish to thank the Atomic Energy Commission for a grant which made the work possible.

Adapters for Introducing Hot Coils into Distillation Flasks for Constancy of Ebullition.

Julian Feldman and Peter Pantages, Synthetic Liquid Fuels Branch, Bureau of Mines, Bruceton, Pa.

The distillation of most substances in an efficient laboratory column at atmospheric pressures offers no problem with respect to the maintenance of constant boil-up rate—a requisite for good column performance. Generally, the addition of fresh boiling chips, at the start of a distillation, is all that is necessary to assure continuous ebullition. However, at reduced pressures, in a conventional boiling flask, it is difficult to maintain smooth boiling, and in consequence, the operating efficiency of the column decreases. A hot wire coil, immersed near the bottom of the flask and carrying an electric current, has been found to be an effective device for controlling ebullition at reduced pressures. Pyrolytic decomposition can be minimized through adjustment of the temperature of the resistance element by means of a rheostat or variable transformer.

In order to introduce these coils into conventional distillation flasks, the authors have used several kinds of adapters made of borosilicate glass with standard-taper or ball and socket joints of convenient size, such as those illustrated in Figures 1 and 2. The metal-to-glass connections are generally tungsten wire No. 16 B.S. gage in uranium glass, although any suitable glass-metal combination may be used (*1*, *2*). The wire leads, silver-soldered to the tungsten, are generally 14- to 16-gage copper. In Figure 2, the leads emerge through small holes in the top of the adapter. A Nichrome wire of 22 gage, approximately 6 inches long, is soldered to the extreme end of the leads.

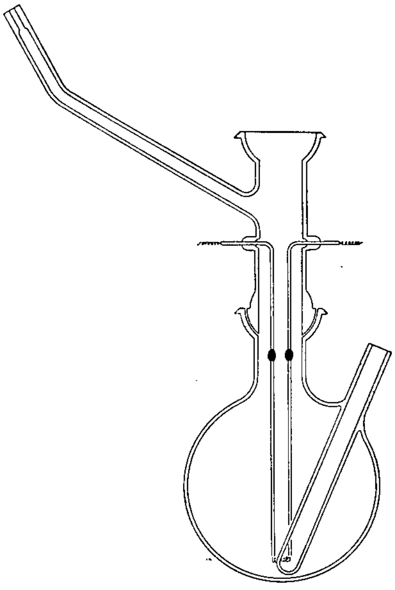


Figure 1

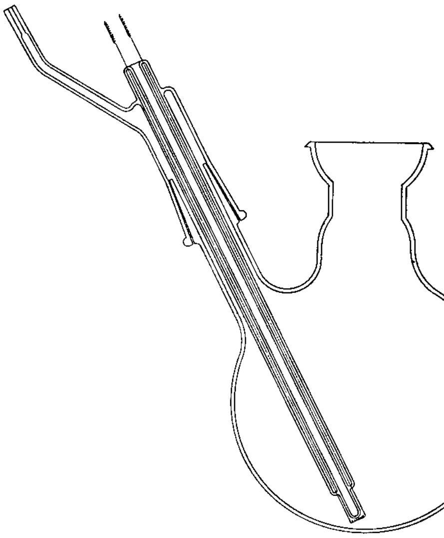


Figure 2

Both adapters serve to connect the flask to the back-pressure manometer. In addition, the side-arm adapter holds a thermowell and may be removed to facilitate introduction of a sample or removal of a residue. These adapters were constructed by F. Joseph Malloy.

LITERATURE CITED

(1) Barr, W. E., and Anhorn, V. J., "Scientific Glass Blowing," p. 116, Pittsburgh, Pa., Instrument Publishing Co., 1949.
(2) Heldman, J. S., "Technique of Glass Manipulation in Scientific Research," p. 87, New York, Prentice Hall, Inc., 1946.

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INSTRUMENTATION

New compilation contains information on more than 500 types of analog transducers, arranged alphabetically according to their functions

by R. H. Müller

THE cathode-ray oscillograph is no longer a mere research tool of great importance; it has already found direct employment in the work of the analyst in at least two applications—in the cathode-ray polarograph and just recently in a commercially available cathode-ray spectrophotometer. No doubt enterprising analysts will develop further uses for this device and it may not be long before its use will be as widespread here as it is in the electronic and general industrial field.

Analog Transducers

The wide utility of the cathode-ray oscillograph has always required suitable transducers for converting various phenomena into an electrical signal which can be delineated on the 'scope. Information on such devices has been widely scattered and it is therefore most timely and fortunate that a compilation of analog transducers is now offered by one of the foremost manufacturers of cathode-ray tubes. The compilation is available from the Instrument Division of Allan B. DuMont Laboratories, Inc., 1500 Main Ave., Clifton, N. J., for 50 cents a copy. The list contains over 500 different types of analog transducers arranged alphabetically according to their functions.

In order to employ the versatility and accuracy of the cathode-ray oscillograph in the investigation of nonelectrical research, development, and industry, it is necessary that the effect in question be converted into an equivalent electrical signal by means of an appropriate transducer. Through the use of the new DuMont compilation, the user may find the model, manufacturer, and mechanical and electrical characteristics of the transducer required.

For each transducer, the following pertinent information is given as available from the manufacturer: function, principle of operation, accessories required, transfer characteristics, power required, amplitude range, sensitivity, output characteristics, band width, resonant frequency, resolution or precision, linearity, weight, range, sturdiness, temperature limitations, mounting, size, remarks, and model designation.

For radiation studies, a special section tabulating Geiger-Müller tubes is included. A transducer accessory listing has also been included, giving characteristics, remarks, uses, and manufacturer. Another section contains pertinent reference material quoting author and date of publication.

Analytical Instrument Clinic

Axel Peterson of the Mellon Institute has given us an interesting outline of the tentative plans for an analytical instrument clinic to be held in conjunction with the Seventh National Instrument Conference and Exhibit at Cleveland, Ohio, September 8 to 12, 1952. The clinic will be sponsored by the analysis instrumentation committee of the Instrument Society of America, of which Peterson is a member. It is planned to exhibit some 10 instruments of the more complex and expensive types, and to have actual working demonstrations combined with lectures on the principles of the instruments and their applications. As the committee's plans are developed, we shall be kept informed of them and will discuss them in this column. As usual, the National Conference and Exhibit will not be restricted to instruments of analytical interest. For several years, this exhibit has been the most elaborate and extensive event of its kind in the country, but it is doubly encouraging to note this specific plan to meet the interests and needs of the analyst.

Organosilicon Coatings on Glass

No doubt most of our readers are familiar with the water-repellent properties of certain classes of organosilicon compounds and the coating of glassware. For those who are not, a most informative and interesting account of numerous applications is given by P. T. Gilbert, Jr., Beckman Instruments, Inc. [*Science*, **114**, 637 (1951)]. Several techniques are described in detail and some of them are directly concerned with instrumental methods of analysis. For one thing, the treatment of glass electrodes with such substances, of which Desicote is an example, eliminates the necessity for rinsing or wiping and, in addition, it has the advantage of improving the electrical insulation and minimizing the leakage. Closely related is its value in preventing the incrustations of potassium chloride from creeping over the surfaces of calomel electrodes. Also,

INSTRUMENTATION

liquid-junction potentials are more readily stabilized in high-precision pH measurements.

Further uses are described in spectrophotometry and flame photometry, in which the cleaning of absorption cells is greatly facilitated, and contamination and carry-over are minimized. The more common operations of analysis, such as pipetting, benefit also by previous treatment with these water-repellent substances. Thirteen references to related investigations are given by the author.

Respirator

A useful device, which should find numerous uses in the analytical laboratory, has been described by J. K. Merlis and J. Degelman [*Science*, **114,** 692 (1951)]. Although designed as an artificial respirator for animal experimentation, it affords an automatic means for alternately admitting air or other gases to a system and connecting the system to exhaust at rates varying between 5 and 40 cycles per minute. It consists of a brass cylinder fitted with a double-ended filleted piston. Lateral motion of the piston opens or closes inlet and exhaust ports with respect to a central system port. Solenoids are wound around each leg of the brass cylinder and these are excited alternately to cause the to and fro motion of the piston. The excitation is controlled by a simple electronic system consisting of a free-running multivibrator. The frequency of oscillation is controlled by ganged potentiometers, and adequate stabilization of the rate is obtained by an OD3 voltage regulator tube. The output pulses from the multivibrator control a 6J5 tube in the anode circuit of which a single-pole double-throw relay serves to switch rectified a.c. to the respective solenoids. The author has suggested a modification in which two 6L6 power tubes can be controlled by

(*Continued on page 24 A*)

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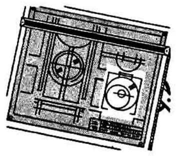

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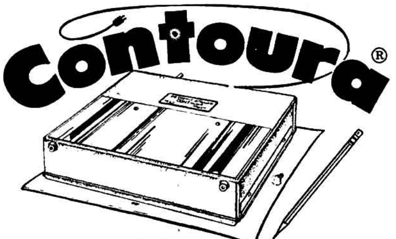

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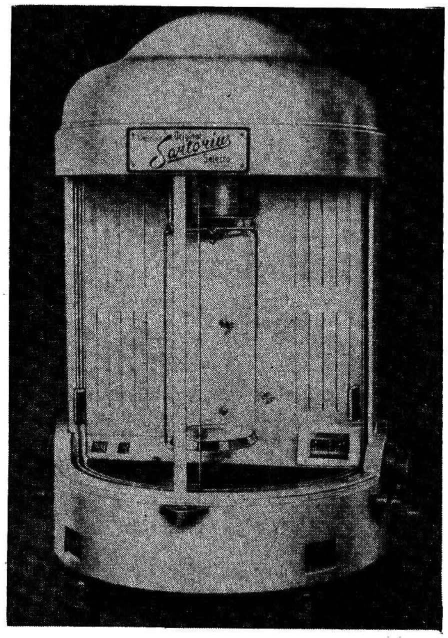

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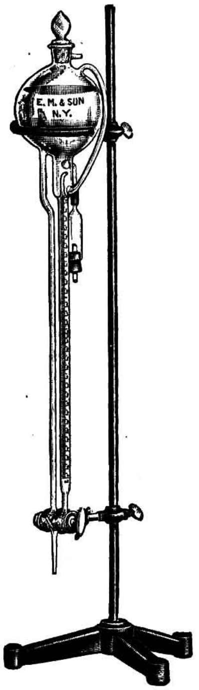

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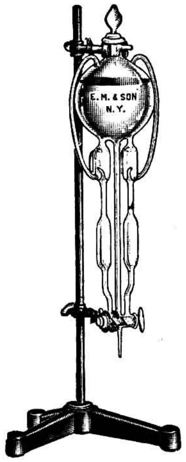

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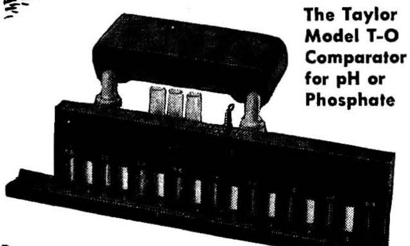
the multivibrator to drive the solenoids directly, thus eliminating the use of a relay.

LSU Symposium

Analysts have come to regard the annual Louisiana State University Symposia on Modern Methods of Analytical Chemistry as an indispensable event on their professional calendar. The fifth meeting, January 28 to 31 was no exception to the rule. Within the diversified program [*Chem. and Eng. News,* **29,** No. 50, 5276 (1951)] several outstanding contributions were of interest to the instrument-minded analyst. Olen Nance gave an excellent resume of the status of high frequency methods. The theory of resonant circuit behavior at megacycle frequencies is complex enough, but the analyst must go beyond this in order to interpret the behavior of substances in such fields in terms of their physicochemical properties. Fortunately, much of this interesting work is currently appearing in the pages of Analytical Chemistry and many of its useful applications will be better understood as a consequence.

W. D. Cooke and Donald DeFord provided additional glimpses of the exciting possibilities in the field of coulometric titrations. The approaches of these two investigators is complementary; the former has been concerned with internal generation of reagents and with supersensitive means of end-point detection. This has yielded analyses for submicrogram quantities, which for precision and sensitivity rival the spectrographic method. The latter is extending the general field of external generation of reagents by coulometric methods with means for completely automatic operation. There are now several accurate procedures which involve nothing more than a precise measurement of current and elapsed time.

Philip W. West has once more served the analyst handsomely in arranging these symposia.

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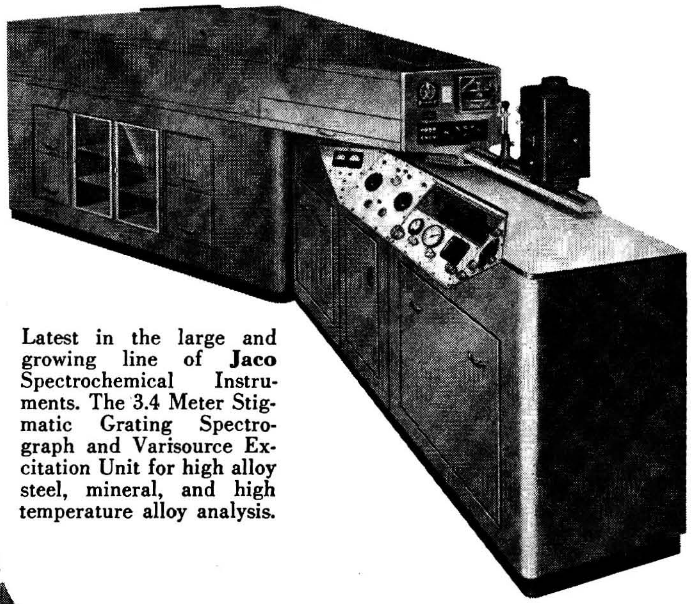

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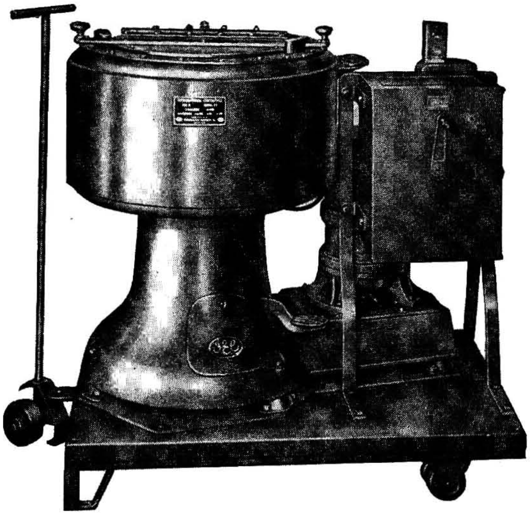

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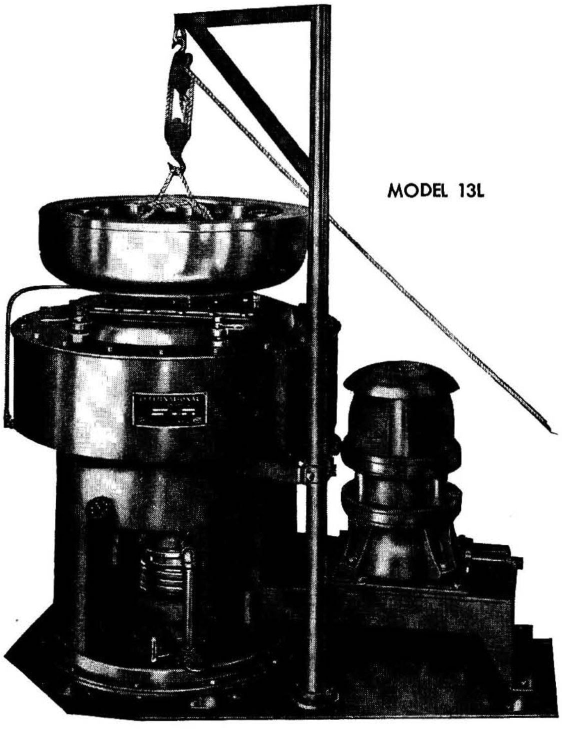

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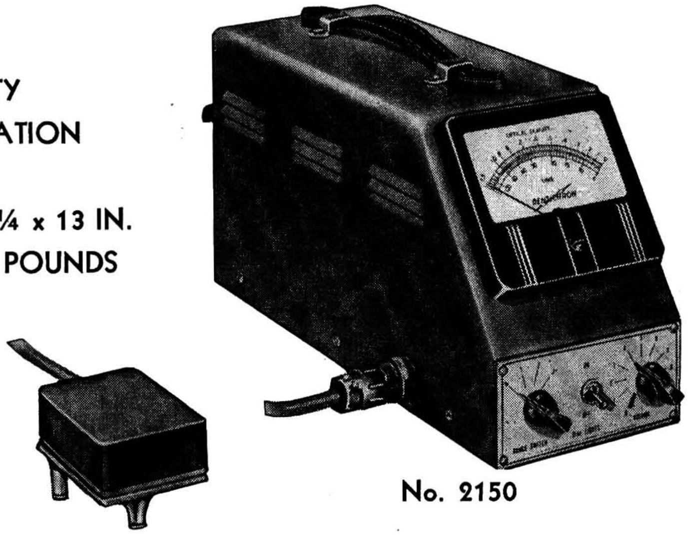

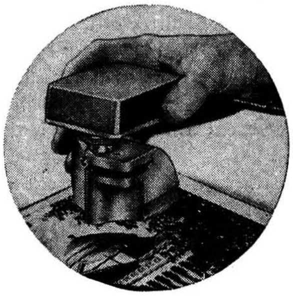

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**See "Quantitative Paper Chromatography for Students" by Patton, A. R., Jr. Chem. Educ. 28, 629 (1951).*

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Aromatic Hydrocarbon Detector

A portable, lightweight aromatic hydrocarbon detector is available from the Mine Safety Appliances Co. The instrument has separate graduations for benzene, toluene, and xylene. In the detector tube, a stain increases in length in direct relation to the aromatic concentration. The cylindrical scale is easily adjusted to bring the zero setting in line with the reagent level in the detector tube. Because the detector tubes can be filled in the field, stability of the indicating material is assured. Twelve tubes can be filled at one time for convenience, and these can be stored for 2 or 3 weeks without loss of sensitivity. Included in the instrument assembly are a color scale, tube rack, mixing bottle, mandrel, 12 rubber tube caps, and a kit for 12 separate tests. The kit contains two vials of granular material, 12 empty detector bottles, and glass cloth swatches. The instrument is supplied in a leather carrying case with shoulder strap. **1**

Vacuum Dryers

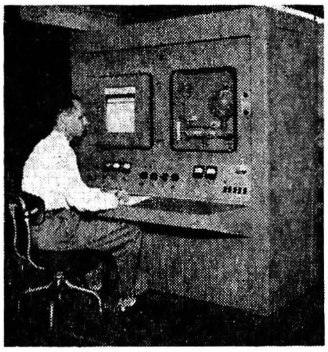
Construction changes in the vacuum shelf dryers offered by the F. J. Stokes Machine Co. permit improved low-cost drying at absolute pressures in the low micron range. Dryer shelves with internal baffles are arranged to provide uniform heat throughout the entire shelf area. The jacketed construction of the top surface of the dryer prevents condensation of the vapors passing toward the vacuum connection. The lower section of the dryer is fitted with a drain gutter and outlet to permit cleaning of the unit without spillage.

The door of the Stokes No. 138 chamber has been changed from cast iron to steel. The B chamber now has two 6-inch sight glasses, while the H and J have three 9-inch glasses instead of the usual 4.5-inch ports. A swivel spotlight, attached to the dryer door, permits close observation of the material during the drying process. This spotlight can be quickly and easily moved to any one of the large glass ports in the door. Swinging eyebolt clamps and handwheels provide easy sealing of the chamber. Specially shaped extruded gaskets fitted into machined grooves in the dryer doors assure a positive seal. The dryers are available in seven chamber sizes, with shelf spacing to suit specific requirements. When necessary, special metals can be furnished, together with metal-sprayed interiors. Steam, hot water, or oil can be used for maintaining various drying temperatures. **2**

Plastic Bottles

Polyethylene bottles manufactured by Plax Corp. are now being used by Beckman Instruments, Inc., as containers for standard buffer solutions. These solutions are available in pH 4.00, 7.00, and 10.00. Each bottle of buffer solution is heat-sealed with a film of polyethylene. In opening a new bottle, the user merely removes the bottle cap, punctures the seal, and squeezes the flexible container. Breakage of the bottles as a result of impact or freezing is eliminated. **3**

Mass Spectrometer



A new model has been added to the line of mass spectrometers manufactured by Consolidated Engineering Corp. This instrument, Model 21-401, is a dual-purpose mass spectrometer designed for the analysis of mixtures of gases and light liquids, as well as for the determination of ratios of stable isotopes. It will fill a particular need in laboratories having moderate analytical loads of a routine nature and will be valuable in research applications involving mixture analysis and stable isotope tracer techniques.

The instrument does not require refrigerants, such as liquid nitrogen. Numerous automatic devices serve to minimize

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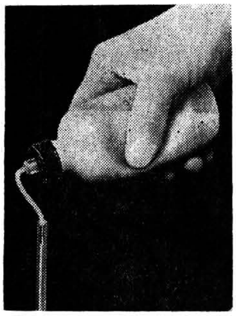
operator errors and thus reduce the time required to carry out an analysis. For mixture analysis, the instrument has a mass range of 2 to 100, with automatic scanning and recording of spectra from mass 12 to 100. About 15 or more complete runs can be made in an 8-hour shift. The spectrum is recorded on a strip-chart recorder, and automatic attenuation of peak magnitudes provides a dynamic recording range of 300,000 to 1.

In isotope-ratio work, the ratio is not only obtained directly by an automatic null balancing method but is also recorded. Within sensitivity limitations, any ratio from 0 to 1 can be measured. The first three decimal places are obtained from decade dials; the last three from the pen-and-ink record. The conversion from mixture analysis to isotope-ratio measurements can be accomplished in a matter of minutes. **4**

High-Purity Mercury

Bethlehem Apparatus Co. is offering mercury specifically for use in instruments requiring a high degree of accuracy. A flexible dispensing tip delivers this mercury directly from an unbreakable 5-pound polyethylene bottle. Transfer containers, spillage, and exposure of the mercury to impurities in the air are thus eliminated. This mercury is said to be superior to standard reagent mercury, remaining bright indefinitely in storage and in instruments. The product, in larger containers, is suitable for use in manometers, polarographs, cathode cells, and other instruments. **5**



Water Purification

Recently developed by Enley Products, Inc., the Demon demineralizer produces pure, demineralized water for only a few cents per gallon in most areas. This unit has been developed for small-quantity users, for whom the usual large equipment would be impractical. Merely by attaching the unit to a regular water tap, the user can produce up to 120 gallons of pure water per cartridge. The demineralizer has an allowable flow rate of up to 30 gallons per hour.

The unit consists of a replaceable plastic cartridge containing resins whose color progressively changes from blue to yellow as the resins become exhausted. The cartridges are removed and replaced when the exhaustion line reaches the bottom. Ionic contaminants are removed from solution by the mixture of anion and cation exchangers. Fiberglas filters help to trap physical impurities.

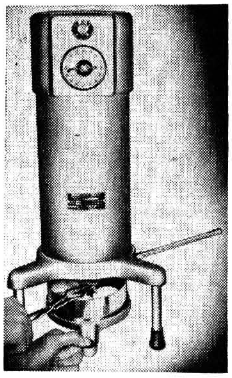
Even if the concentration of dissolved salts in a particular water supply is high, the unit can reduce this concentration to less than 0.1 p.p.m. A complete unit costs $14.95, and the replaceable cartridges cost $5.50 each, with a $1.00 credit allowed for each exhausted cartridge. **6**

Stopcock Adapters

Three sizes of stopcock adapters—small, medium, and large—to cover the full range of laboratory stopcocks have recently been introduced by the Emil Greiner Co. The small size adapter covers the range of 2- to 4-mm. stopcocks; the medium size covers 6 to 8 mm.; and the large size, 10 to 15 mm. These adapters are designed for laboratory workers who require pressure stopcocks for burets, gas sampling, measuring apparatus, and other applications. Manufactured completely of corrosion-resistant materials, they eliminate the annoyance of leaking stopcocks and the high cost of special pressure stopcocks. **7**

Moisture Determinations

The Model 276-S offered by Harry W. Dietert Co. may be used for drying a wide range of samples. The unit is equipped with a thermostat having a range of 150° to 300° F. The temperature may be controlled to within 7° F. of the selected temperature. The heating element is of heavy Nichrome wire. The outer housing is well insulated from the heating element, thus ensuring a relatively cool outer surface.



Sample pans, either 1 or 2 inches in depth, may be used. Unlike previous models, this unit is equipped with pans made of stainless steel rather than aluminum. As many as three samples contained in a 50 × 25 mm. dish may be dried at one time. The unit's efficient ventilation accelerates the drying process. **8**

Storage Cabinet

A new storage cabinet for radioactive samples has been developed by Nuclear Instrument and Chemical Corp. A major feature of this cabinet, Model N4, is its provision for replacing sample holders or the sample holding tray in case of con-

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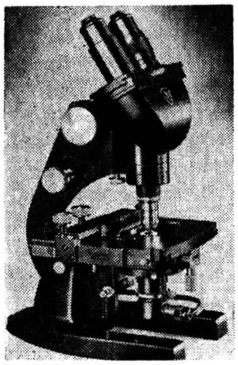
tamination. Sample holders are plastic cups which are pressed into holes in the tray. If contamination occurs, these cups are easily replaced at little cost to the user. The cabinet is provided with 10 drawers, each containing 10 sample holders. The holders permit samples of many different sizes to be held, and each one within its drawer is numbered for convenience and reference. A dust-tight cover may be placed over the cabinet to eliminate the possibility of contamination of the samples. **9**

Filter-Paper Electrophoresis

A filter-paper electrophoresis apparatus is available from Kelab Ab, Sweden. The migration of protein molecules occurs in a filter-paper strip soaked with buffer solution. When adequate separation has occurred, the various protein components are fixed and stained. The dye bound to the protein is eluted and measured colorimetrically. An electrophoresis curve can then be constructed. This technique requires only about 1 to 2 mg. of protein, or about 0.01 to 0.03 ml. of serum. The apparatus, which includes two Plexiglas electrode vessels with platinum electrodes, requires 110 to 240 volts a.c. input and has a continuously adjustable output of from 50 to 315 volts d.c. **10**

Microscopes

New dark-field microscopes, combining the latest mechanical features with an improved illuminating system, have been announced by American Optical Co. These instruments permit the study of small particles which have a refractive index and color similar to the surrounding medium. These particles are not ordinarily seen in the bright field of standard microscopes. In the new instruments, the light source may be properly centered in relation to the condenser optics. The condenser may be adjusted for slide thicknesses of from 1.15 to 1.25 mm. A special 97X oil-immersion objective is supplied with a built-in iris diaphragm to eliminate the need for a funnel stop.



Either monocular or binocular instruments may be selected. Both have hinged substages that open to facilitate cleaning. The pinch-grip mechanical stage permits the slides to be interchanged without disturbance to the stage settings. Compared to older models, the focusing is smoother and easier, wear is reduced, and backlash is eliminated. The binocular bodies are lightweight and dustproof, and have inclined converging eye tubes for comfortable posture and reduced eyestrain. **11**

Oxygen Indicator

A new, improved indicator is now being offered by Mine Safety Appliances Co., for use in measuring the oxygen content of inert and combustible atmospheres. The instrument is available in the standard full-scale ranges of 0 to 1%, 0 to 5%, 0 to 10%, and 0 to 25%. The instrument includes a large meter having 50 scale graduations. This permits the direct reading of oxygen concentration to within 2% of the selected scale range.

The heart of the indicator is the detector cell—essentially a primary cell with a metallic and a hollow carbon electrode immersed in an electrolyte. In operation, the sample to be analyzed is passed through the hollow carbon electrode of the detector cell. Hydrogen evolved at the carbon electrode causes polarization of the cell, which manifests itself in a decrease of the generated voltage and current. Oxygen from the sample diffuses through the wall of the carbon electrode and combines with the hydrogen, producing a depolarization effect. Consequently, the more oxygen the sample contains, the higher is the electric current generated by the cell.

The current delivered by the cell is affected by variations in the cell temperature. To eliminate this effect, the cell has been placed in a thermostatically controlled water jacket which is maintained at a constant temperature of approximately 30° C.

The entire instrument is contained in a metal case, 13.5 × 17.25 × 10 inches, suitable for either surface or flush-panel mounting. The indicator is designed for permanent installation and continuous operation. The power supply is normally 110-volt, 60-cycle, single-phase a.c. **12**

X-Ray Diffraction Scales

In chemical analysis by x-ray diffraction methods, the rapid and convenient determination of $\sin^2 \theta$ values or interplanar spacings from powder photographs may be made with the new, improved transparent scales offered by Nelson P. Nies. Each set of scales is for one radiation and camera diameter and consists of five or six scales which cover a range of 1% in film length. The scales are graduated in both directions from the 0° and 90° centers to allow convenient centering of the film. The following sets of scales are now available: for 57.3-mm. camera diameter, *d*-values for iron or copper radiation; for 114.6-mm. diameter, *d*-values for cobalt, copper, chromium, iron, or molybdenum radiation; and for 143.2-mm. diameter, *d*-values for iron or copper radiation. **13**

Beta Emitters

Atomic Instrument Co. has announced the availability of sets consisting of five beta-emitting reference sources. These sets include carbon 14, cobalt 60, thallium 204, bismuth 210, and protactinium 234. Their beta energies range from 0.155 to 2.3 m.e.v. A manual indicating characteristics and methods of calibration is supplied. This set provides a convenient method for determining the beta efficiencies of various radiation detector units, such as Geiger tubes, scintillation phosphors, and electroscopes. By comparison with these calibrated sources, it is possible for millicurie determinations to be made with numerous beta-emitting radioisotopes. Additional mounts and copper disks are provided for such determinations. **14**

Annular Lamp

Heitz and Lightburn announces a new annular lamp for close-up photography. The lamp, consisting of a ring of small electric bulbs, can be installed around any camera lens and provides shadowless illumination of sufficient light value for color or black-and-white film. A special rheostat permits the light to be dimmed or turned on full, depending on the individual problem. With the aid of a circular opaque plate inserted on top of the lamp and a concave mirror installed underneath, the lamp also provides an object table for illuminating small objects from behind—a valuable feature for scientific photography. **15**

Laboratory Centrifuge

The new, low-priced, angle-head centrifuge introduced by Scientific Glass Apparatus Co. is recommended for applications where fast individual tests are required. To protect the operator and prolong the life and usefulness of the unit, all rotating parts are concealed by an aluminum guard with an opening at the top, fastened by screws to the base. Three large suction feet are provided for additional safety and smooth operation.

The unit has four openings to receive four standard 15-ml. metal shields supplied with each centrifuge. Four 15-ml. glass tubes are also provided. The centrifuge is powered by a 115-volt, 60-cycle motor, operated at 1550 r.p.m. The outside diameter of the centrifuge is 9.75 inches at the base, and the height is 8.5 inches. The shipping weight is 18 pounds. **16**

Voltmeter Shunt

A new shunt has been introduced by Keithley Instruments for use in connection with its Model 200 vacuum-tube electrometer—a d.c. voltmeter with a high input impedance. The shunt permits the quick conversion of the electrometer to a micromicroammeter. Available in any one of seven standard resistance values, the shunt permits d.c. readings from 10^{-6} to 10^{-13} ampere. The device clips over the guard ring of the electrometer, and no other connections are necessary. **17**

MANUFACTURERS' LITERATURE

Nefluoro-Photometer. A 16-page booklet explains the theory behind three methods of analysis (colorimetry, fluorometry, and nephelometry) and describes the operation of a new precision instrument combining all three of these techniques in a single electronic-optical system. The Nefluoro-Photometer gives rapid readings for a wide range of inorganic and organic compounds. Fisher Scientific Co. **18**

Petroleum Products. A 4-page bulletin features new specifications and technical data on petrolatums, white oils, petroleum sulfonates, and special petroleum products. Pennsylvania Refining Co. **19**

Radioactive Materials. Six basic fields in which radioactive materials may be used in the solution of industrial problems are outlined in recent issue of company house organ, *Tracerlog.* Tracerlab, Inc. **20**

Instrument Amplifier. A 4-page bulletin describes Model 102, a bridging amplifier with an extremely high input impedance. The instrument is used to increase the accuracy of vacuum-tube voltmeters and oscilloscopes employed with high-impedance circuits. The bulletin includes complete specifications and diagrams of typical applications. Keithley Instruments. **21**

Color Control. Technical report, "Color Control in Paper Making," indicates the many factors that may influence the color of the final paper product. Suggestions are given for controlling these factors to ensure uniform results. American Cyanamid Co. **22**

Copper and Lead Analysis. A 20-page manual outlines various methods for the analysis of copper and lead by electrochemical methods. These procedures, as well as the booklet's extensive bibliography, are a product of research at Battelle Memorial Institute. Eberbach Corp. **23**

Pyrometers. A 28-page booklet describes company's line of Radiamatic pyrometers. These instruments, in which voltages are generated in proportion to the temperature of the object sighted upon, are specifically designed for measuring the temperature of moving objects, for use where vibration and shock may break the usual thermocouple, for use in corrosive atmospheres, and for measuring temperatures above the thermocouple range. Booklet includes sections on operation, theory, constructional features, engineering specifications, accessories, and typical applications. Minneapolis-Honeywell Regulator Co. **24**

Laboratory Apparatus. Bulletin provides information on ammeters, voltmeters, Geiger counters, thermometers, transformers, barometers, and other equipment. Herbach and Rademan, Inc. **25**

Research Laboratories. Company's laboratories are described in profusely illustrated booklet. Research on catalysts, polymers, petroleum, and plastics is covered. M. W. Kellogg Co. **26**

Aluminum Stearates. Illustrated booklet describes history, manufacture, and properties of aluminum stearates used in lubricating greases. The evaluation of lubricating greases is discussed in detail. American Cyanamid Co. **27**

Laboratory Apparatus. Catalog provides information on pH meters, automatic titrators, power supplies, buffer tablets, colorimeters, photonephelometers, spectrometers, centrifuges, and other apparatus. Wilkens-Anderson Co. **28**

Metal Identification. A 48-page booklet outlines procedures for the identification of more than 125 metals and alloys. Table lists nominal chemical compositions of many such materials. International Nickel Co. **29**

Scientific Instruments. Bulletin 300 describes and illustrates various types of pH meters, titrators, spectrophotometers, and accessories. A Geiger counter, gamma detector, flow colorimeter, and micromicroammeter are also covered. Beckman Instruments, Inc. **30**

Glassware. Comprehensive 190-page catalog discusses company's laboratory glassware, including beakers, bottles, condensers, cylinders, desiccators, distillation apparatus, flasks, ground joints, tubes, and other equipment. Corning Glass Works. **31**

Instruments. A 60-page booklet describes x-ray diffraction equipment, monochromators, goniometers, diffraction cameras, Geiger tubes, spectrometers, and other apparatus. North American Philips Co. **32**

Fluorescent Lamp. Booklet gives information on the J-H1 fluorescent mercury lamp, which produces a golden-white light. Booklet provides complete tables of technical and transformer data. Westinghouse Electric Corp. **33**

Radiation Instruments. An 8-page bulletin contains details on 10 nuclear radiation detectors, including a scintillation counter, boron-coated counter tube, step-motor impulse counter, and alpha hand counter. General Electric Co. **34**

Caustic Soda. Company offers a new expanded and revised 84-page booklet, entitled "Caustic Soda—Properties, Solutions, Unloading, and Handling." Booklet contains many revisions and additions, including new tables, illustrations, and charts of precautions in handling. Solvay Sales Division. **35**

Industrial Instruments. A 28-page catalog, No. 5000, describes wide assortment of pyrometers, potentiometers, level meters, thermometers, thermocouples, pressure gages, switches, starters, relays, and motorized valve assemblies. Minneapolis-Honeywell Regulator Co. **36**

Geon Resins. Technical details on the compounding of Geon 101 and 101-EP polyvinyl chloride resins are contained in 16-page bulletin. Analysis of these materials is indicated. B. F. Goodrich Chemical Co. **37**

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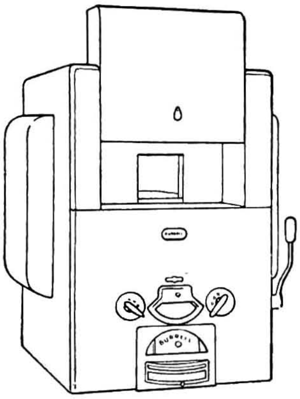

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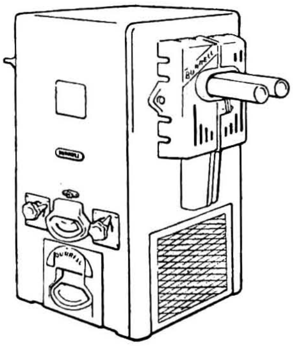

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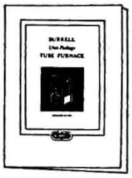

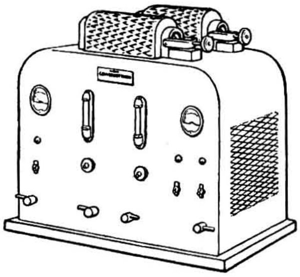

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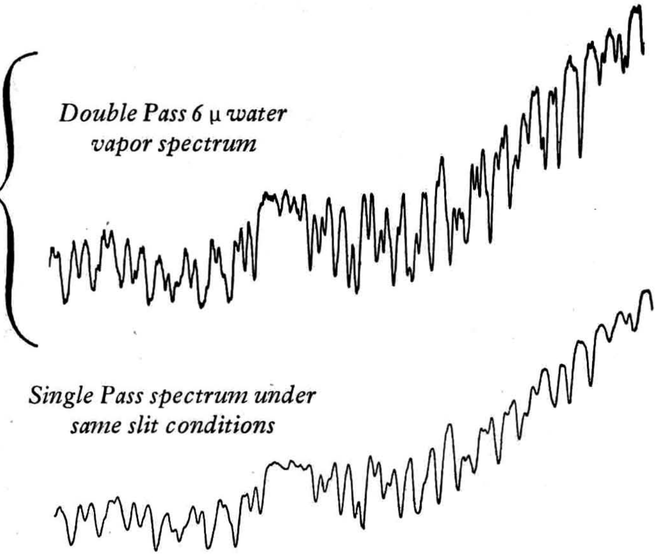

Double Pass 6 μ water vapor spectrum

Single Pass spectrum under same slit conditions

The Double Pass Infrared Spectrometer permits performance hitherto unobtainable in small prism instruments

The Model 112 Perkin-Elmer Infrared Spectrometer incorporates the new Model 99 Double Pass Monochromator, permitting double monochromator performance with a *single* optical system. By passing radiation twice through the same optical system, double monochromator performance is achieved with a minimum of mechanical complexity and at a cost comparable to single monochromator instruments.

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The Model 112 is otherwise similar to the well-known Perkin-Elmer Model 12-C Infrared Spectrometer. All Model 12-C accessories are usable with the Model 112. Existing Model 12's may be converted to double pass operation.

Write for Bulletin 102 containing a complete description of Model 112.

FEATURES

Resolution: Better than 2.0 cm^{-1} with suitable prisms.

Scattered Radiation: Less than 0.1 percent throughout the range.

Range: 1-40 microns (with suitable prisms). May be used in visible and ultraviolet with special attachments which can be provided.

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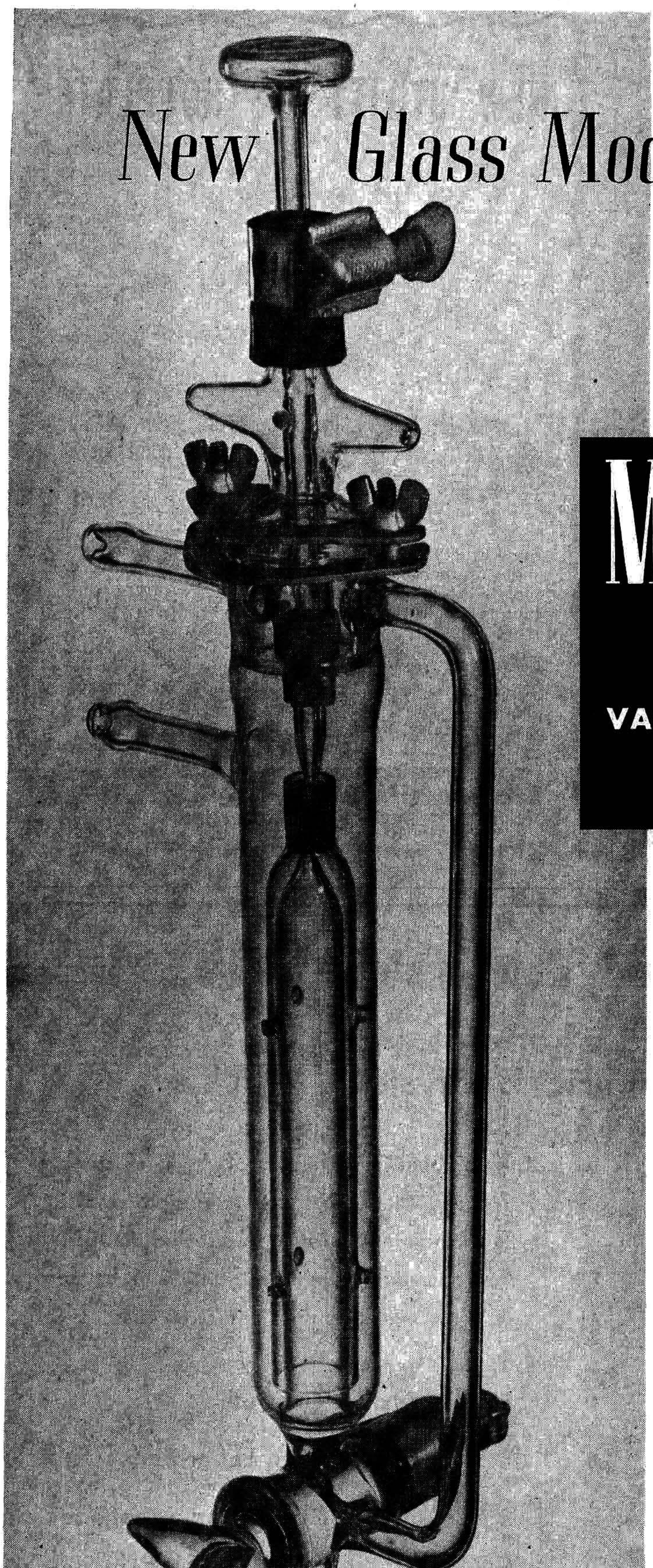

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This glass model is especially suitable for laboratory applications because of its corrosion resistance.

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The operation is based on sealing off a given amount of gas inside the diver at the control pressure. The sensitive diver responds to the slightest increase in pressure in the system which causes the diver to drop and open the upper orifice which is connected to a source of pressure lower than the control pressure. This allows the excess gas to leave the system and restore it to the control point. A small bleed into the system from a source of higher pressure insures that the pressure in the system will never go below the control pressure.

When operated under vacuum, the quantity of gas maintaining the control pressure is sealed inside the diver even when the system is restored to atmospheric pressure, since the excess pressure forces the inside seat of the diver down upon the orifice of the internal central tube and prevents breaking of the mercury seal.

*For Theory of Operation See Following Article:
Gilmont, R., Ind. Eng. Chem. Anal. Ed. *18*, 633, (1946); *23*, 157 (1951).

PRICE LIST:

G15071 Cartesian Manostat #7, all glass model ready for use with rubber connections. Clamps for pressure operation and mercury not included. ea. **$39.50**

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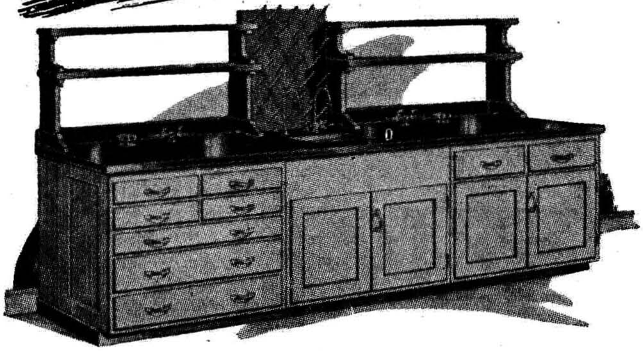

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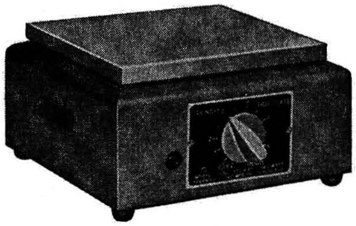

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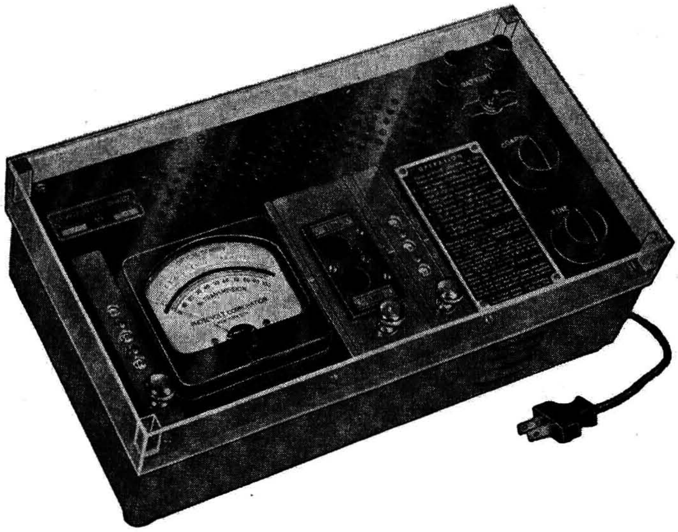

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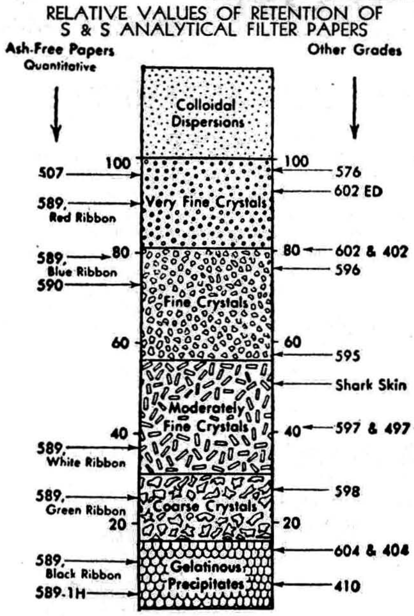

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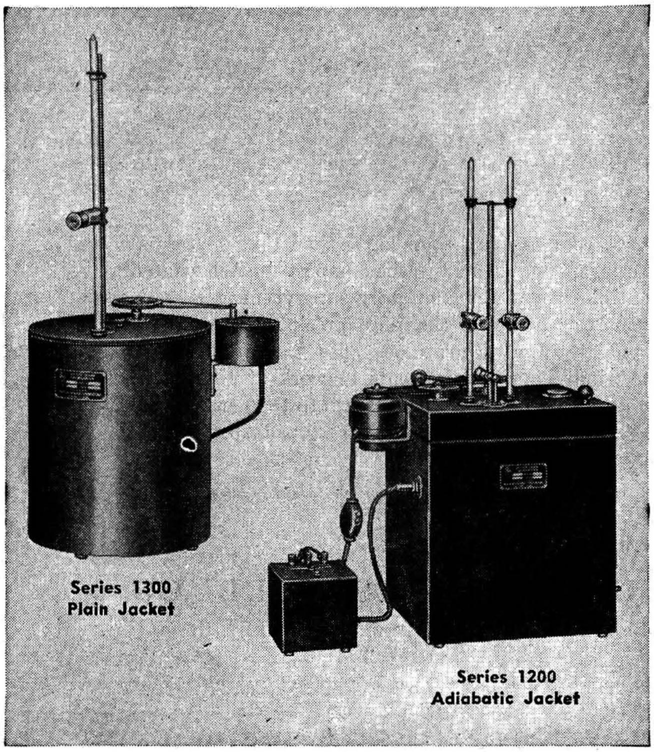
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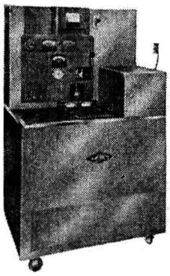

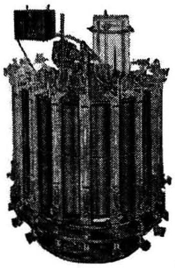

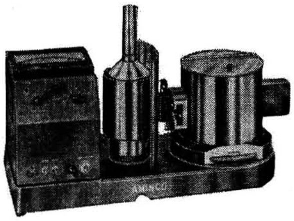

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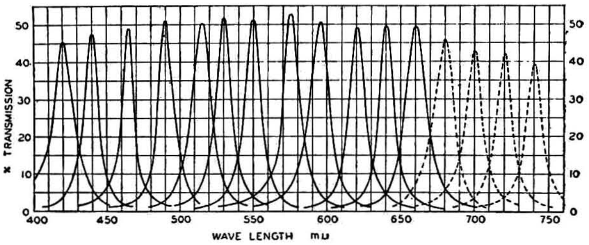

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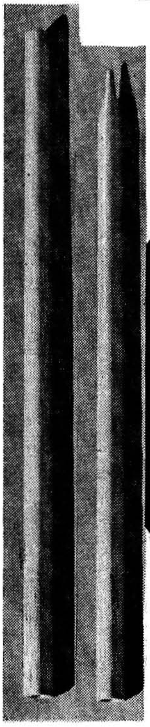

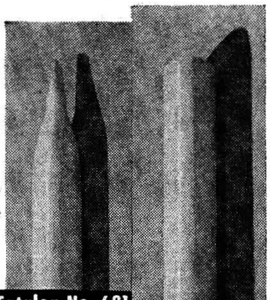

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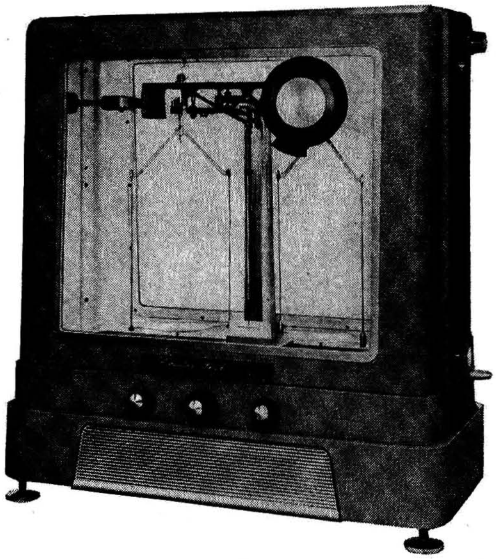

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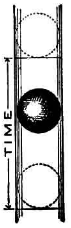
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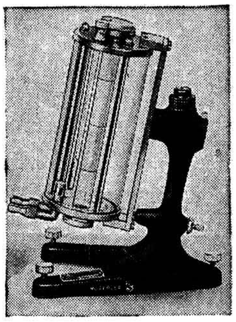

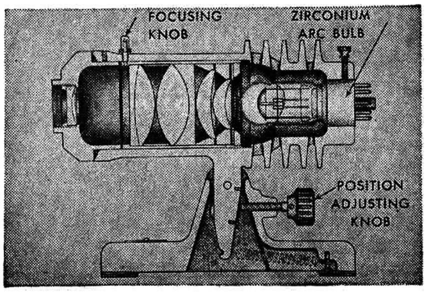
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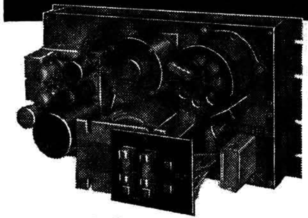

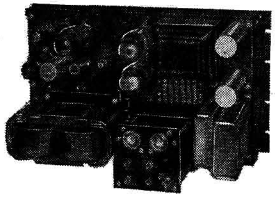


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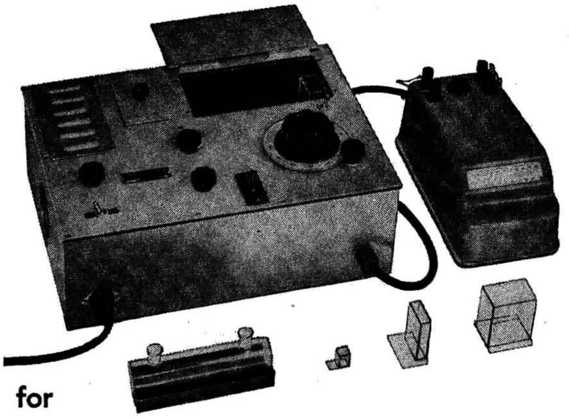

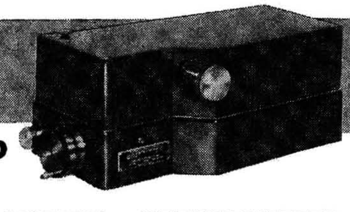


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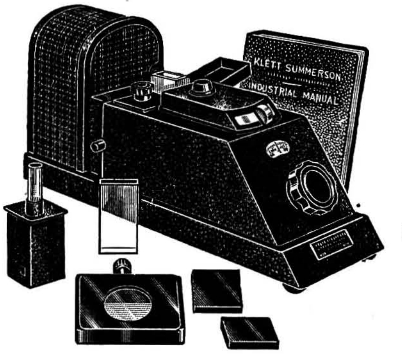
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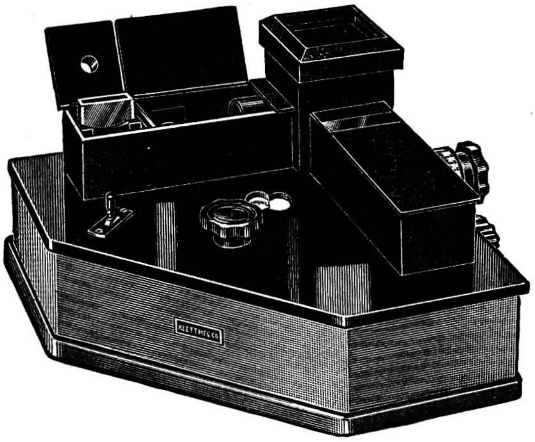

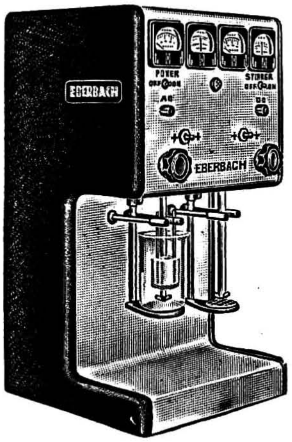
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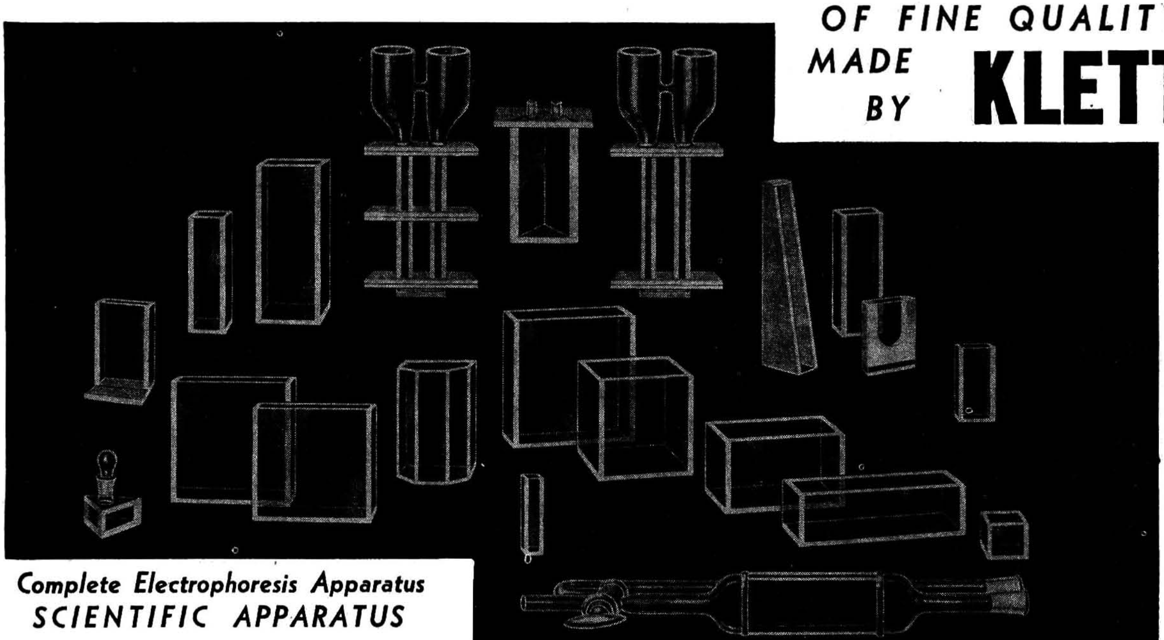

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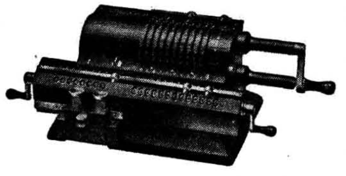

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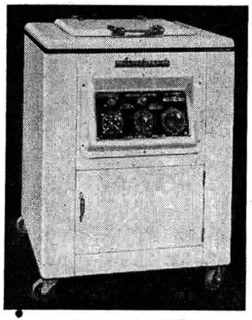

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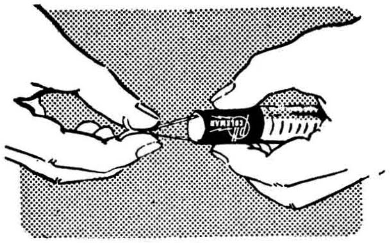

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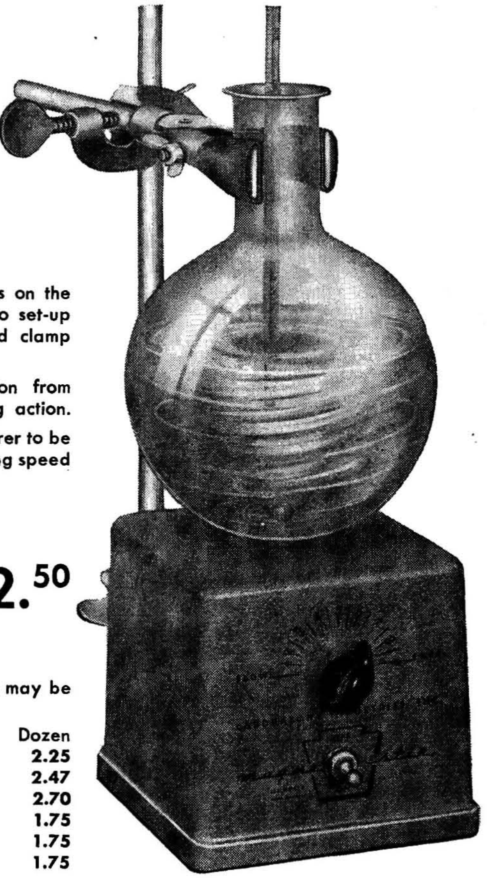

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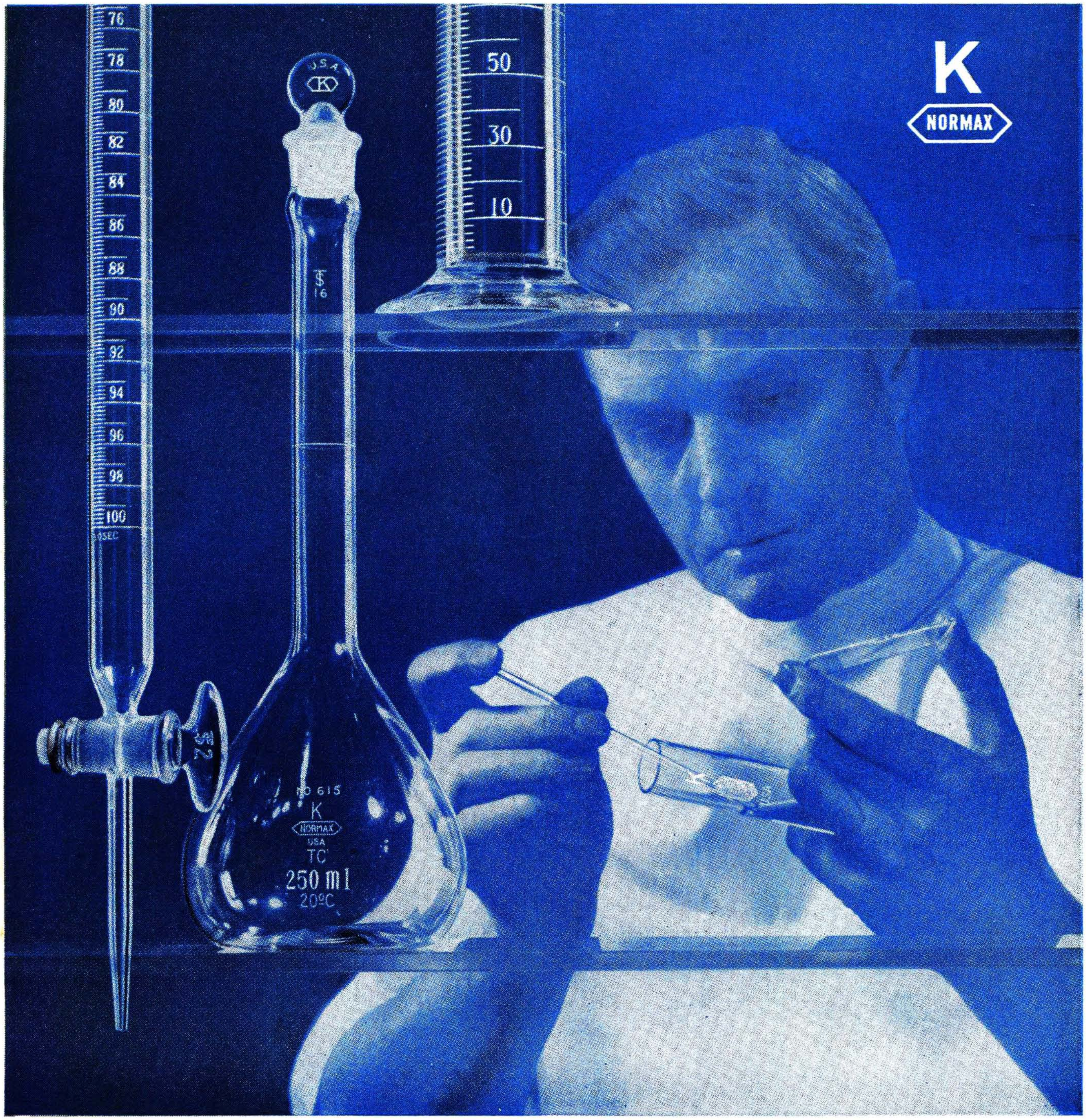

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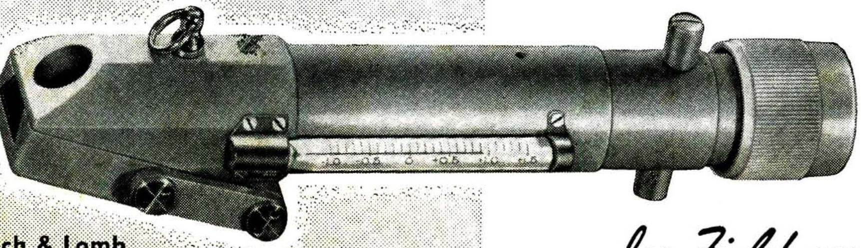

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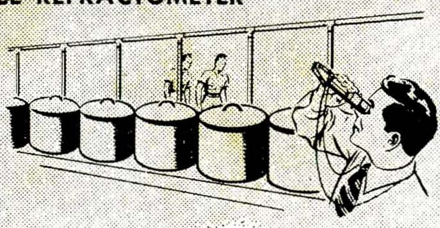

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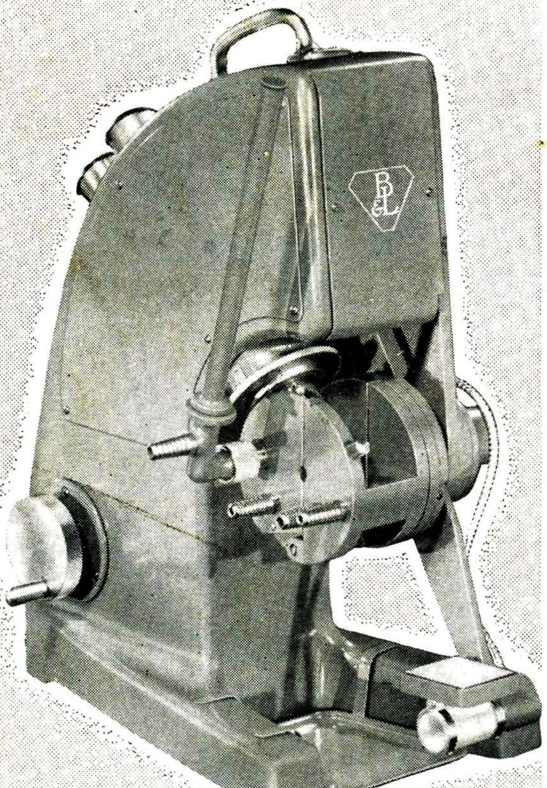

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