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ANALYTICAL CHEMISTRY



The analytical chemistry of the "less familiar elements" becomes more familiar as research and development quicken industrial interest in these elements and their compounds



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This Month's Cover. The so-called "less familiar elements" may soon have to get a new name. They are getting more and more familiar as research teams explore their characteristics and find new uses. The stimulus of nuclear physics and chemistry, development of semiconductors in electronics, the role played by minor elements in nutrition, production of better alloys and metals—all of these have accelerated interest in the less explored areas of the periodic table. More and more chemists have been confronted with analytical problems of the less familiar elements. Recognizing this, the ACS Division of Analytical Chemistry devoted its Sixth Annual Summer Symposium to the subject. The papers presented there appear in this issue beginning on page 1580.

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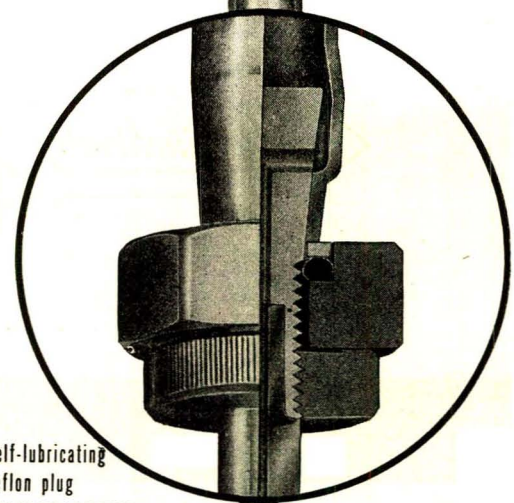
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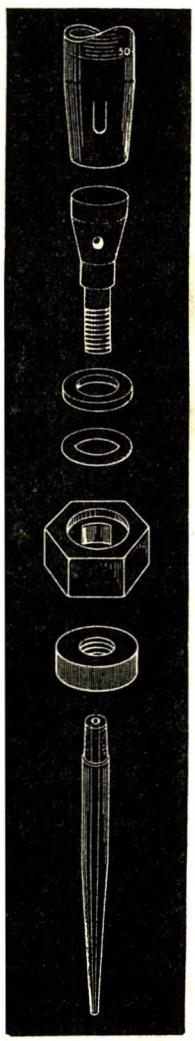


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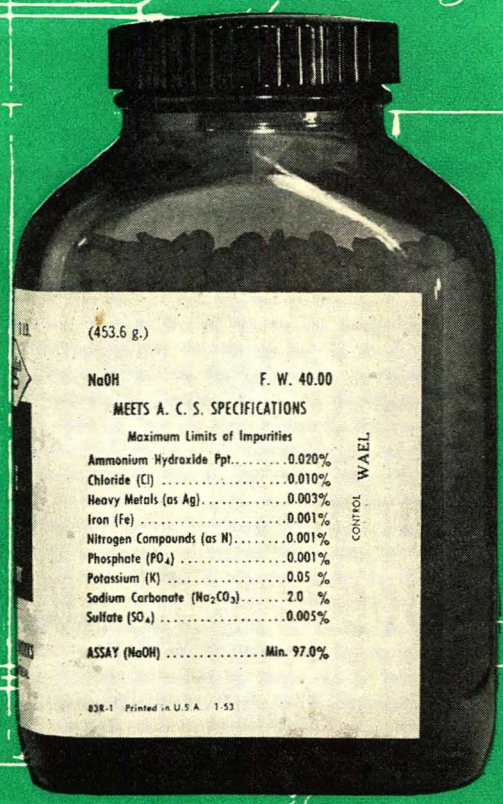
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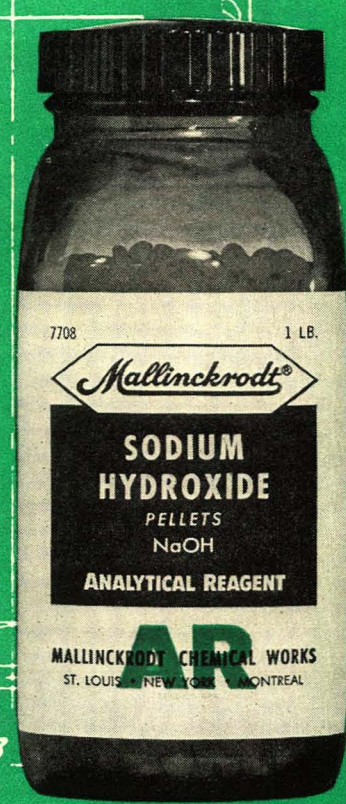


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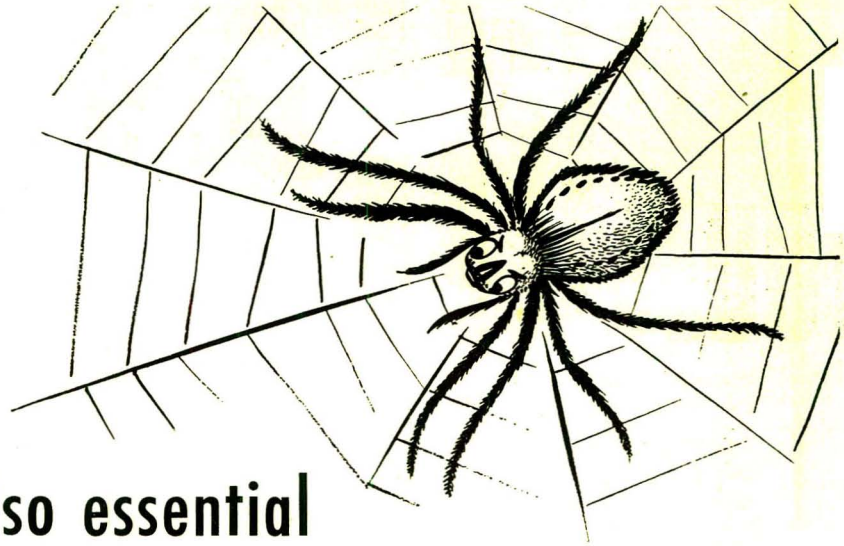
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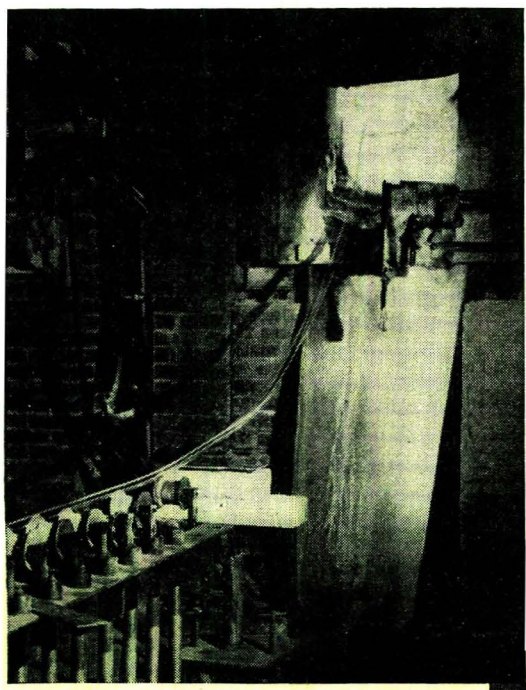
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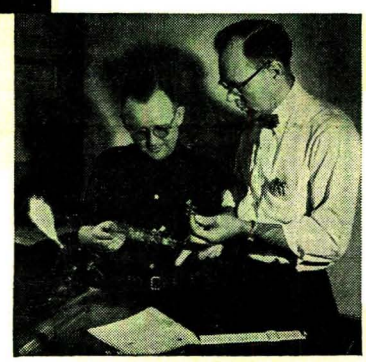
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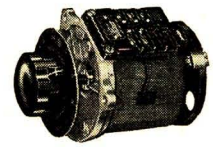
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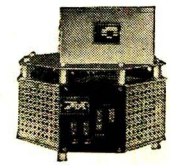
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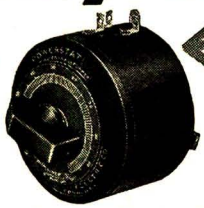
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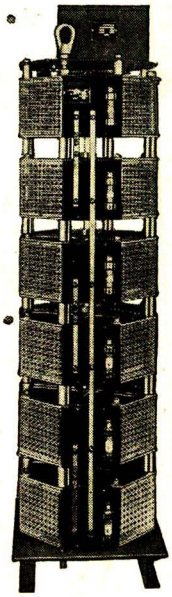
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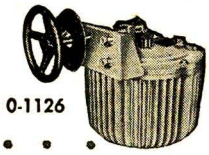
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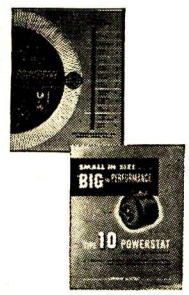
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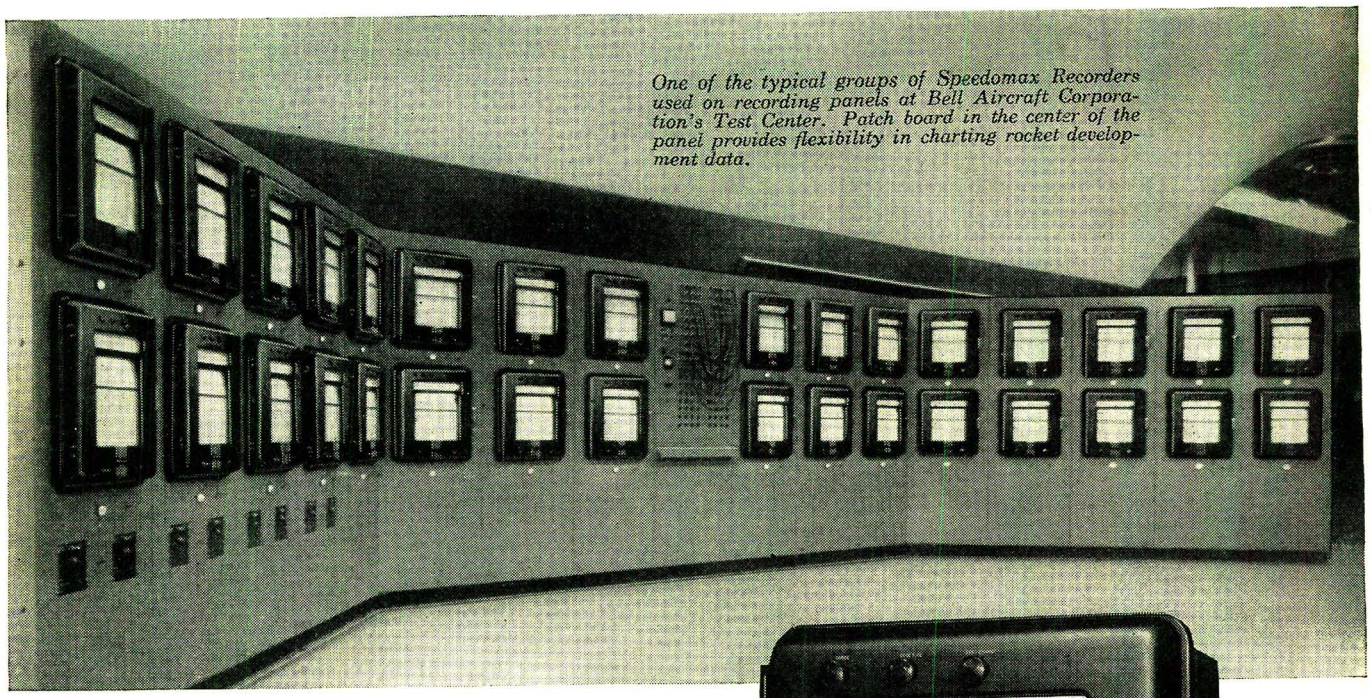
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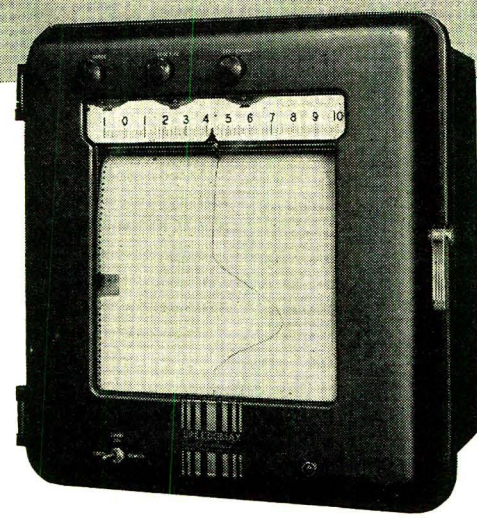
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One of the typical groups of Speedomax Recorders used on recording panels at Bell Aircraft Corporation's Test Center. Patch board in the center of the panel provides flexibility in charting rocket development data.



Just set the knobs at top of instrument for the desired range and zero, and this AZAR recorder is adjusted to your exact specs . . . spreads any millivolt value from one to twenty across the full chart width, for measuring Force, Weight, Temperature, Speed, Voltage or any condition which yields an electrical recorder signal.

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Kimble makes Thermometer history!



This magnified photograph shows two thermometers after two minutes' immersion in boiling 4% solution of sodium hydroxide. Notice how the filler has been eroded from the one on the right. Notice how fused-in filler is unaffected in the new thermometer on the left.

At last! Graduations that really defy chemical attack!

Now, after years of experiment, Kimble's researchers-in-glass have developed a new, permanent, fused-in filler for etched-stem laboratory thermometers. This new filler is as resistant to chemical attack as the glass itself.

Here are thermometers designed to stay legible. The filler is fused-in, and can never erode. The durable markings are unaffected by attack of organic materials and acids (except hydrofluoric). Resistance to alkalis is as great as the glass itself.

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In laboratory tests, instruments were immersed in acids, and organic solvents at elevated temperatures over long periods of time. Test conditions were more stringent than any likely to be encountered in actual use.

Every Kimble thermometer is individually retested for accuracy . . . thoroughly processed with special attention to suspension rings and reservoir bulbs where residual heat strain is one of the most common causes of breakage.

Economical to use

Permanent filler plus special processing assure a long lifetime of hard laboratory usage. Because Kimble thermometers stay in service longer they cost less than ordinary etched-stem thermometers.

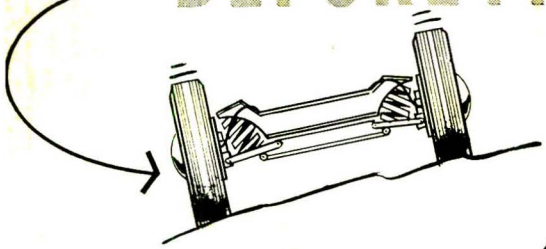
These new Kimble Exax thermometers are made in a variety of ranges, including those specified by the American Society for Testing Materials.

Your Kimble laboratory supply dealer has these new, permanently marked Kimble thermometers in stock now. Consult him on your requirements.

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Toledo 1, Ohio—*Subsidiary of Owens-Illinois Glass Company*

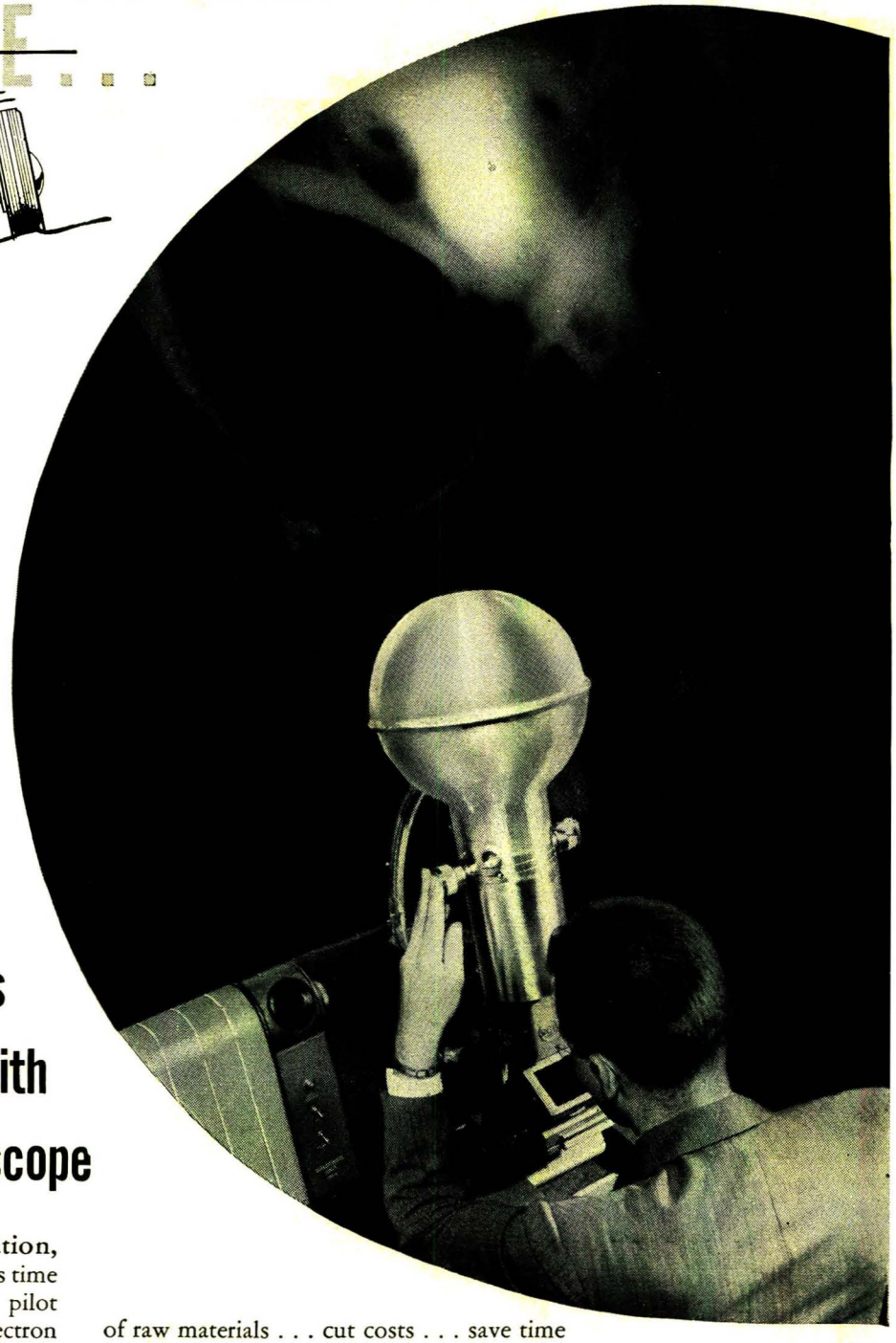
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NOW . . .

Socony-Vacuum's pilot plant cuts testing time to a matter of minutes—often eliminates several weeks' output of unusable product. The RCA Table Model Electron Microscope contributes substantial time savings to this operation—permits specimen testing in just a few seconds. (In background, microphoto of suitable batch.)



Socony-Vacuum cuts weeks to minutes with RCA Electron Microscope

In a new quality-control operation, Socony-Vacuum Oil Co. now eliminates time lags—and wasted production—in a pilot operation built around the RCA Electron Microscope Model EMT-3. With this equipment, Socony-Vacuum research men actually cut weeks of test time to the few minutes required to prepare and photograph a sample.

For a small investment Socony-Vacuum has obtained the dual advantages of electron-microscopy—high resolution and high magnification (40,000 X photographically).

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on the RCA Electron Microscope (EMT-3) and RCA's training assistance program, write Scientific Instruments, Dept. 11W, Radio Corporation of America, Camden, N.J.

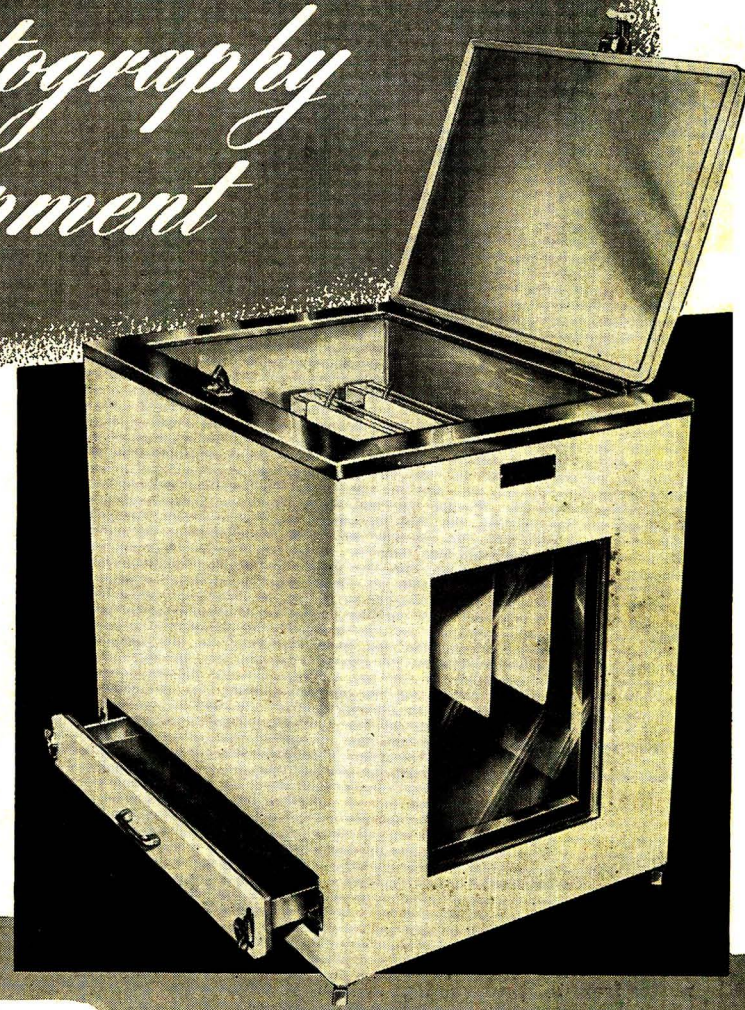
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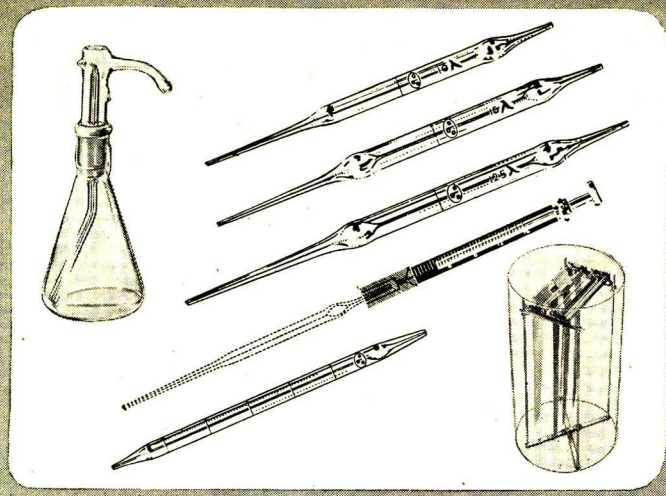


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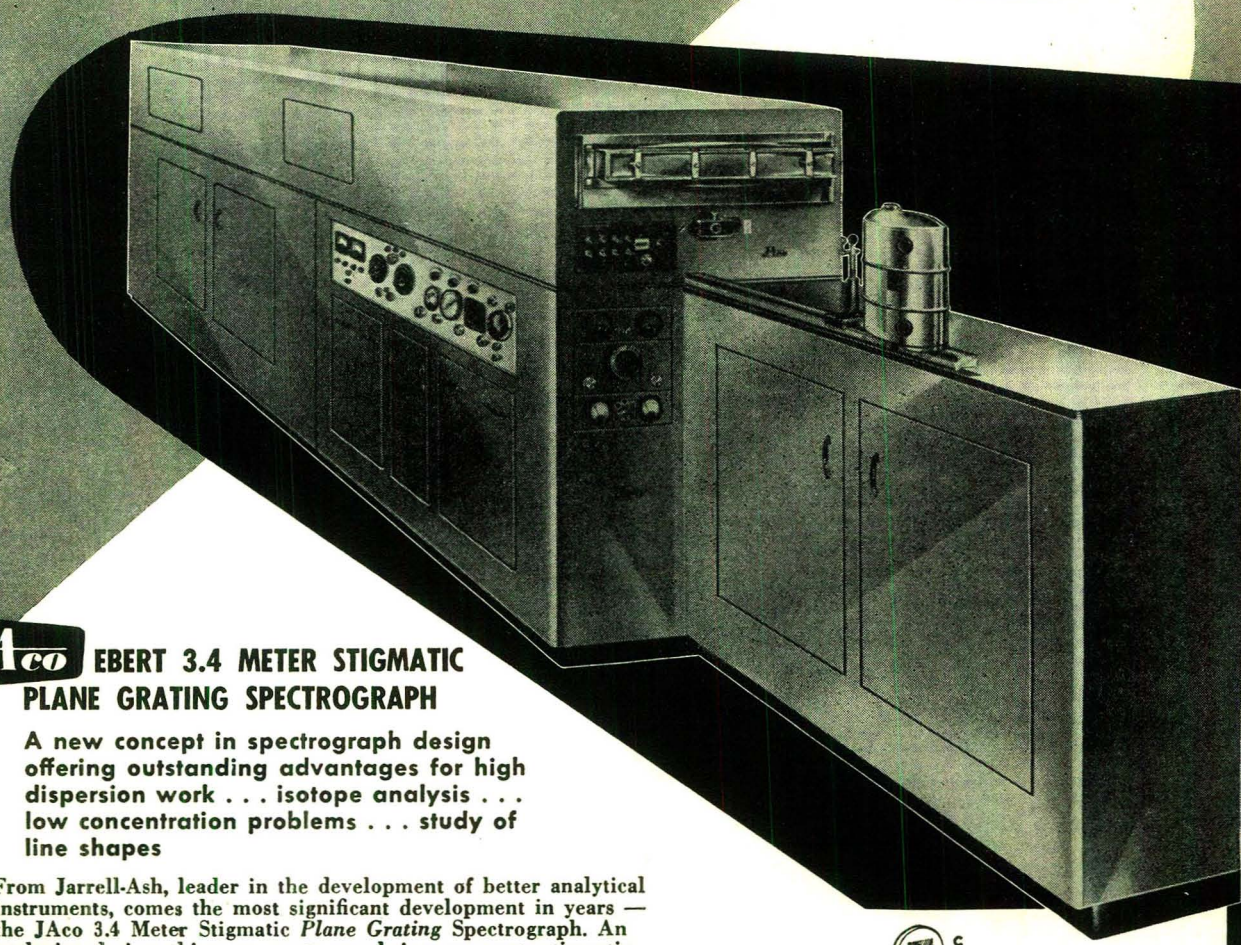
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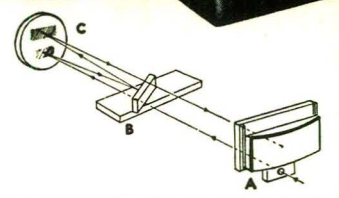
A new concept in spectrograph design offering outstanding advantages for high dispersion work . . . isotope analysis . . . low concentration problems . . . study of line shapes

From Jarrell-Ash, leader in the development of better analytical instruments, comes the most significant development in years — the JAco 3.4 Meter Stigmatic *Plane Grating* Spectrograph. An exclusive design, this new spectrograph is a compact, *stigmatic* instrument specifically developed to produce ultra-high dispersion and resolution while covering 2000A to 6500A *at a single setting.* Theoretical resolving power of this outstanding spectrograph ranges from 75,000 in the first order to 600,000 in the eighth order. Resolution is guaranteed to be 100,000 at 3000A while the practical speed equals the famous JAco Wadsworth Grating Spectrograph.

Normally the JAco Plane Grating Spectrograph is supplied with an original 15,000 line/inch grating. But for special applications 7500 line/inch or 30,000 line/inch gratings are available — or all three may be supplied on a Kelvin type mount or on an interchanger nosepiece.

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For complete information on the ways this significant new instrument can help you, write for illustrated catalog EB10-53 today.



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In the JAco Plane Grating Spectrograph the light from the slit (A) passes under the plane grating (B) to a large mirror (C) which renders it parallel and reflects it back to the grating. The light returned by the grating consists of parallel bundles of rays for each wavelength, the separate bundles at diverging angles in accordance with the dispersion of the grating. These rays strike the upper part of the concave mirror, which now acts as a camera mirror to focus the rays on the plateholder, back above the slit.

With this simple optical arrangement the wavelength range is easily changed by rotating the grating — angles as high as 45° to 50°, which produce first order spectra up to 25,000 to 30,000A, are practical.

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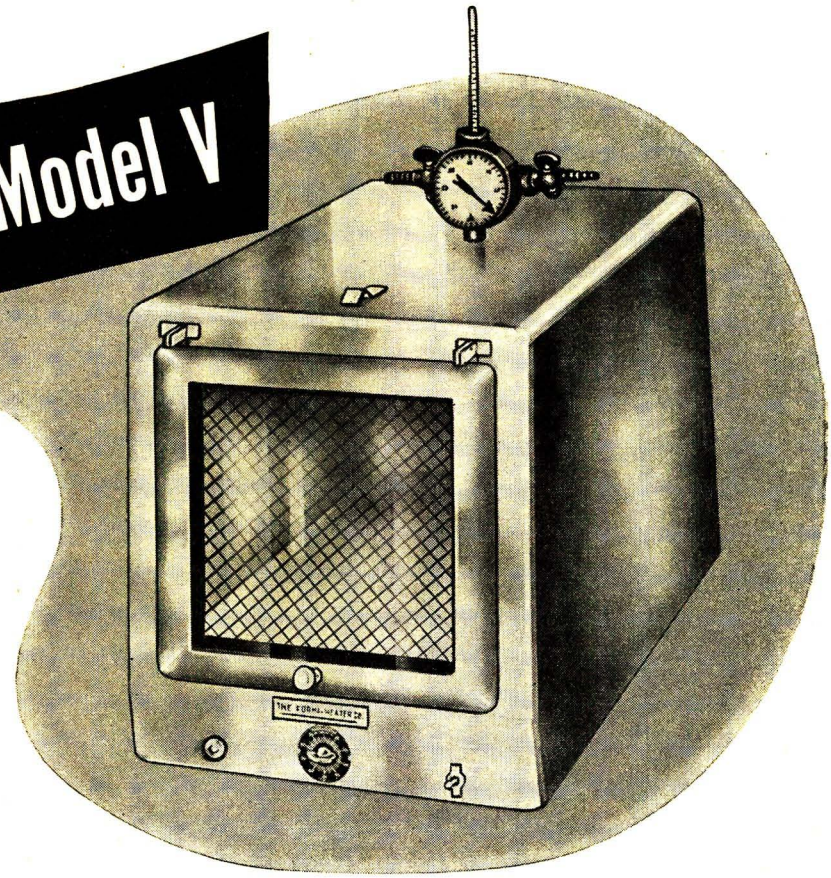
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Heavy wire mesh protective screen over rugged tempered Pyrex door window insure safe visibility.

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All controls are located where the operator can see and use them with minimum of lost time.

★ **Door Swings Up and Out of Way—Better Seal**

★ **Vacuum Valves**
Nickel plated vacuum needle valves with serrated hose connections. One valve for vacuum and one for dry air or gas flushing.

★ **Ruggedly Built—Designed To Last**

★ **Vacuum Chamber—Special ⅛" Welded Steel Construction**

★ **Wall Heat Infra-Red Completely Surrounds Chamber**
This more efficient heating method eliminates electrical connections inside the chamber.

★ **New Type Laminated Insulation To Minimize Heat Loss**

★ **White Interior—Finished With Special High Temp Catalyst Paint**

★ **Unique Heater**
New type woven heating element contains close to 700 feet of resistance wire to bring wattage density to an absolute minimum.

★ **Loading Space**
740 cubic inches—all usable.

★ **¼-Inch Thick Neoprene Door Gasket—Self Seating**

★ **2-Inch Thick Glass Wool Insulation Completely Surrounds Chamber**

★ **All Controls On Front Panel**

SPECIFICATIONS

Over-all size 12″ w x 17″ d x 15″ h
Working chamber 8″ w x 15″ d x 7″ h
115 V, 60 cycle, AC, 650 watts, Single phase
Exterior lug for grounding
Temperature range Room to 125 degrees C.
Finish silver gray hammerloid

INFORMATION FOR ORDERING

H-52829—Vacuum Oven Complete with 3″ diameter standard vacuum gauge, one expanded metal shelf equipped with thermometer bracket, two valves, rubber feet, neon pilot light, line switch, two-wire cord and plug. Net weight, 37 lbs. Price—**$155.00**

The Forma-Vac Model V was designed from scientific field surveys. Before work was started on this new vacuum oven full consideration was given to safety and to delicate drying operations conditioning and annealing problems and many other utility drying operations.

It is considered to be of prime importance from the safety standpoint that the heating elements are located outside the vacuum chamber. Of course, this accomplishes the factor of "cleaning up" the vacuum chamber to give more usable space as well as greater uniformity of heating. The entire chamber wall acts as the heater for the inner chamber area. Over 475 square inches of actual heating surface with the low wattage density factor completely eliminates any "hot spots" insuring chamber temperature uniformity, optimum control and stability.

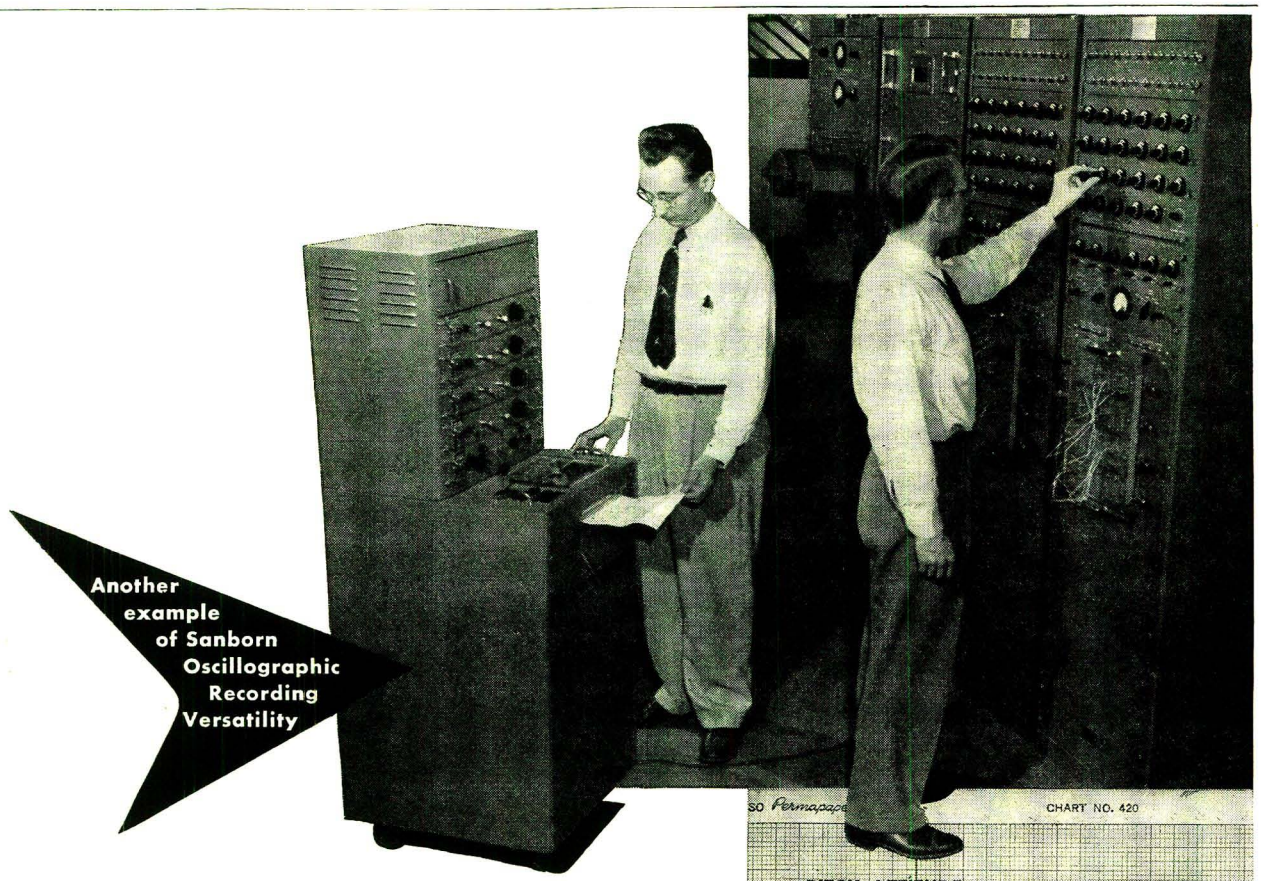
By the most critical standards and rigid safety requirements of certain large research organizations there is nothing better, stronger, and safer than Corning's tempered Pyrex glass. The Forma-Vac utilizes a one-half inch thick plate of this glass enclosed in a special cast aluminum door. This door is swung upright on the new easy-view sloping front for the purpose of saving table space so that when the oven is open the door is up and out of the way. This also enables the user to adapt the oven for ordinary heating problems when vacuum is not required. When door is swung down into position it naturally closes the chamber without necessity of catches or latches to hold it in place.

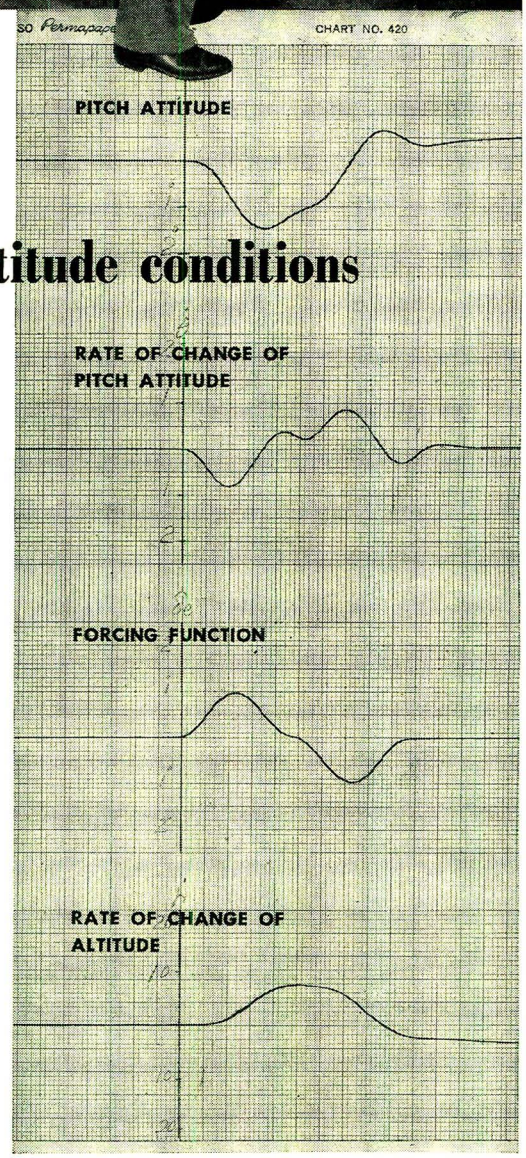
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At Eclipse-Pioneer, engineers make good use of Sanborn 4-channel recording systems in conjunction with high precision analogue computers to establish performance criteria for automatic flight systems and components.

At other laboratories Sanborn Systems are being used to record such phenomena as: stress, strain, pressure, displacement, thickness, velocity, acceleration, current, voltage, temperature, torque, light, flow, force, load, position, rpm, radiation and tension.

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Sanborn Systems are widely used because of the availability and ready interchangeability of amplifiers and preamplifiers, as well as such Sanborn advantages as: inkless recording in true rectangular coordinates, high torque movement, time and code markers and wide choice of paper speeds. In addition, a basic choice of systems, 1-, 2-, and 4-channels, provides a system to fulfill almost any laboratory requirements.

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Sanborn Company
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the analyst's column

AT THE 1952 fall meeting of the AMERICAN CHEMICAL SOCIETY in Atlantic City, the Division of Cellulose Chemistry held a Symposium on Molecular Weight and Molecular Weight Distribution of Cellulose. This symposium appears in the November 1953 issue of *Industrial and Engineering Chemistry*. Two of the papers are committee reports of interest to many of our readers. Abstracts are given below, together with page number where the complete report appears in *Industrial*.

Report of the Cellulose Disperse Viscosity Subcommittee. A. F. MARTIN, Chairman. Page 2497.

The Cellulose Disperse Viscosity Subcommittee has been operating for several years under the auspices of the Division of Cellulose Chemistry of the AMERICAN CHEMICAL SOCIETY and the Chemical Methods Committee of TAPPI. Within the past year, ASTM Subcommittee D-23 has joined the sponsoring organizations. The work has been furthered in particular by a financial grant from TAPPI for work done by B. L. Browning of the Institute of Paper Chemistry.

Dr. Browning has completed a study of the solvent power and stability of cupriethylene and cuprammonium solvents as a function of the amount of copper and of base. Work is being started on the preparation of cellulose solutions in the optimum solvents and on the viscosity behavior of such solutions.

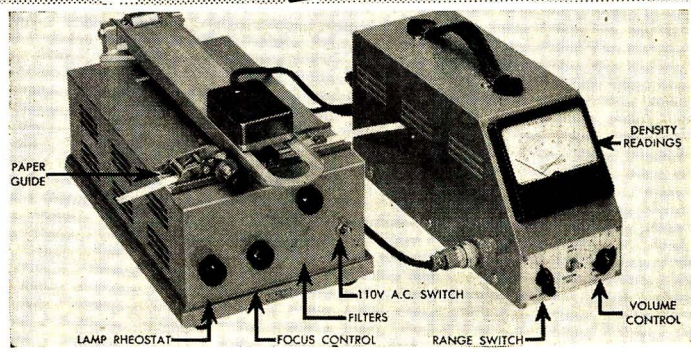
The Viscosity Subcommittee is at present considering a tentative method in which results will be reported in terms of intrinsic viscosity and/or intrinsic fluidity. Conversion factors to degree of polymerization (DP) will be included. Viscosity measurements will be made at a concentration such that the product of concentration and intrinsic viscosity equals 3.0. Preliminary data indicate excellent reproducibility at a level within 10% of the true intrinsic viscosity.

This tentative method is being tested in several laboratories, but a choice of solvent should be made before a standard method is published.

Precipitation and Fractionation of

(Continued on page 19 A)

A Superior TRANSMISSION DENSITOMETER for QUANTITATIVE PAPER CHROMATOGRAPHY combines the Welch DENSICHRON® with Transmission Light Source



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The special Welch Transmission light source with a filter paper guide for holding and advancing the papergram at 3 mm increments, when used with the Densichron becomes a complete transmission densitometer for quantitative paper chromatography. The quantitative analysis of complex compounds such as PROTEINS, SUGARS, VITAMINS, etc., has been simplified by reading maximum densities of papergrams with the DENSICHRON.

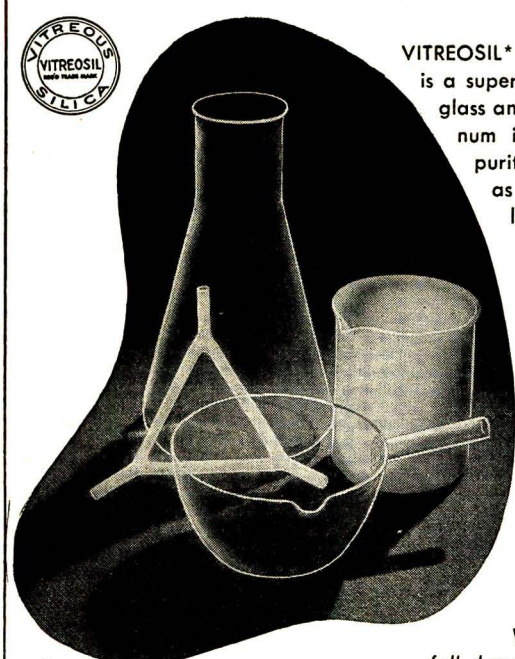
This new apparatus and procedure will speed up your work and permit the analysis of very small samples. Works equally well for quantitative paper electrophoresis.

This instrument will be shown at the 24th Annual Exposition of Chemical Industries in Philadelphia, November 30 to December 5, 1953. See it at our Booth No. C-42.

Write for literature describing the production of papergrams and the use of the Densichron for quantitative determination by the maximum density method. **$425.00**

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facts on Infrared *for the laboratory*

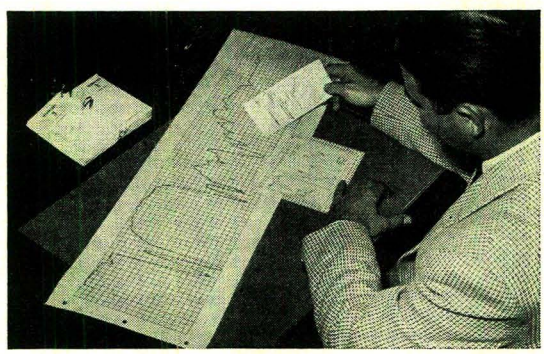
How to record Infrared Spectra directly on { *IBM CARDS* / *MC BEE CARDS* / *API PAPER*

What size spectra do you need for your infrared spectra library? Chances are you can record spectra directly on whatever size sheet you have standardized on, if you have a Perkin-Elmer Model 21 Infrared Spectrophotometer.

Pictured here are spectra recorded directly on standard chart paper (20 x 76 cm), on a Mc Bee card (12 x 14 cm) and on an IBM card (7 x 14 cm). Another size possibility is API paper. Intermediate and smaller size paper may also be used.

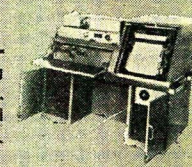
On most Model 21's no special attachments are needed. Change-gears provided as standard equipment are used to select the proper abscissa scale while the beam trimmer adjusts the ordinate. A simple attachment for changing the ordinate without loss in energy will soon be standard on new instruments and available as an accessory for older models.

This is one more example of the value of versatility in infrared instrumentation obtainable only from Perkin-Elmer equipment.

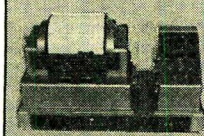


By means of simple change-gears, various-sized spectra can be recorded directly with the Model 21.

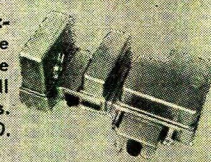
The ONLY complete range of infrared instruments and accessories to meet all research needs!



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

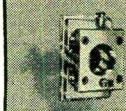


Model 21 Double Beam Infrared Spectrophotometer—The fastest and most efficient instrument commercially available for the recording of large numbers of spectra. Records directly in percent transmission. *Write for Bulletin 104.*



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

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



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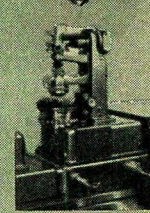
Pressure Cells—for liquids or gasses; path lengths from 0.025 to 50 mm, pressures up to 300 psi. Useful in trace absorption or overtone work. Long and short sizes.



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



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

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Cellulose Nitrate. Report of Subcommittee 21, Committee on Standards and Methods of Testing, Division of Cellulose Chemistry, ACS. R. L. MITCHELL, Chairman. Page 2526.

Subcommittee 21 of the Committee on Standards and Methods of Testing has been in operation since 1949 with the objective of selecting a method for the determination of molecular weight distribution of cellulose which could be adopted as an ACS standard. Seventeen different laboratories have applied their preferred fractionation procedures to some or all of six standard celluloses which were made available through the chairman of the subcommittee. A majority preference has been shown for "precipitation" fractionation of the cellulose nitrate derivative, prepared with minimum degradation. At the 119th national ACS meeting (Boston, 1951), it was decided to prepare a tentative standard method for this procedure as one specific fractionation method, limited in scope but giving useful and reproducible data. It is not claimed to be absolute in its values or ideal for all situations. A questionnaire was used to obtain a number of opinions in developing the method which is now presented for general consideration. Three operations are described:

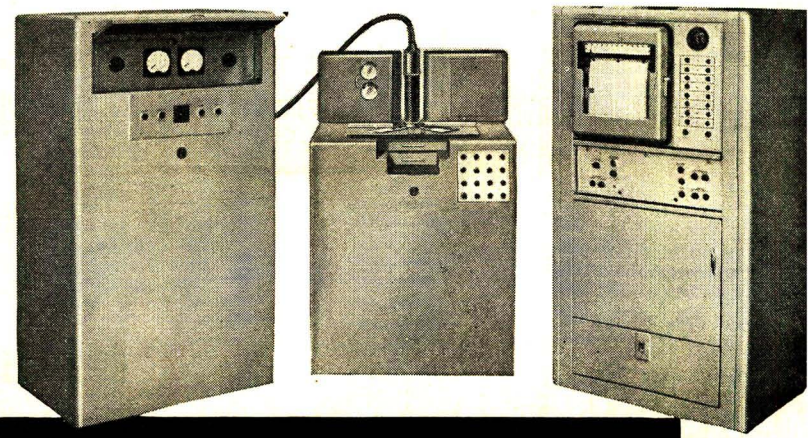
1. Conversion of the cellulose to cellulose nitrate
2. Separation into several fractions through stepwise precipitation from solution by addition of a nonsolvent
3. Measurement of the weight and viscosity of each recovered fraction and calculation of its average chain length.

CHEMISTS are versatile and practice many of the arts as amateurs. While this corner has always stuck to prose, because flights of poesy never come to our addled brain, we would like to pass on to you proof that we have versatility among our readers—to wit, Norris F. Hall of the University of Wisconsin, who is provoked to poetry by the following quotation from the outline of a lecture on "Errors in Quantitative Analysis":

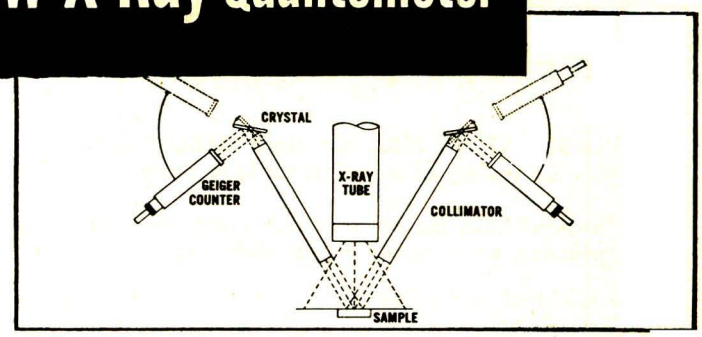
"IV. Indications of the existence of instructional error.
A. ...
B. Inability of many competent students to achieve the inherent error of the method.
C. ..."

Read the sad story of competent Joe
Whose working errors were always low.
He toiled and slaved till he lost his reason
But was always dogged by high precision.
He died a prey to chronic terror,
For he never achieved the inherent error.

Science Editor



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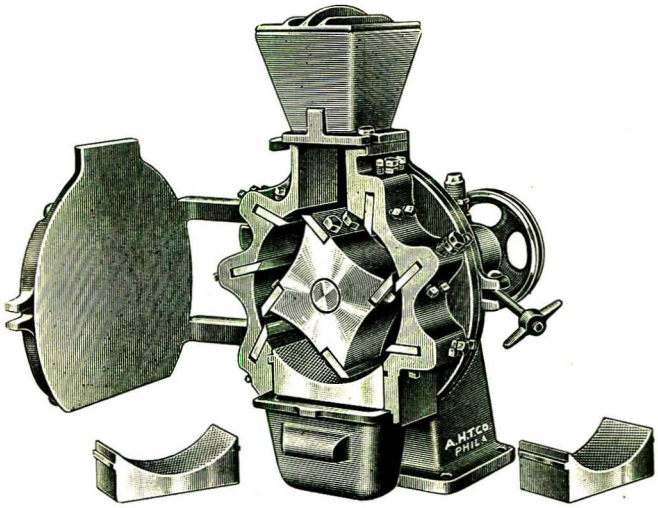
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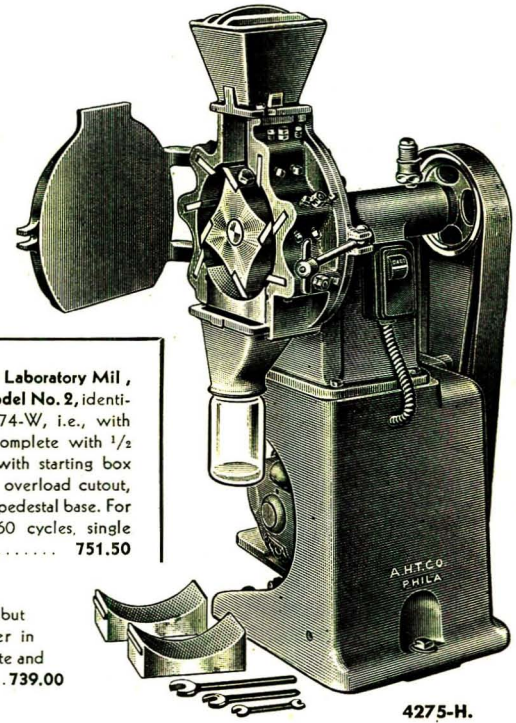
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4274-W. Wiley Laboratory Mill, Standard Model No. 2, as above described, with chute — as shown in illustration of 4275-H — three 16 oz. glass jars with plastic caps, and three sieves of 0.5 mm, 1 mm and 2 mm mesh, respectively. With pulley for V-belt, and set of wrenches for adjusting knives, but without drawer or motor..... **433.00**

4275. Ditto, but with drawer in place of chute and glass jars, without motor..... **420.50**



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4275-H. Wiley Laboratory Mil, Standard Model No. 2, identical with 4274-W, i.e., with chute, but complete with ½ h.p. motor with starting box and thermal overload cutout, mounted on pedestal base. For 115 volts, 60 cycles, single phase, a.c..... **751.50**

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ANALYTICAL CHEMISTRY

Walter J. Murphy, Editor

The Responsibility of the Author

AN interesting study would be to determine the number of new authors each year whose names appear on the contents pages of AMERICAN CHEMICAL SOCIETY journals.

We have never made such a study, but we suspect the figures would be very high. The size of the profession has grown tremendously in the past decade or two and it is self-evident that the amount of research conducted continues to grow by leaps and bounds.

The growth, of course, means that in any given year we are dealing with a crop of new authors who may not be familiar with the manuscript reviewing system used by ACS editors.

A very comprehensive discussion of the system was published as an editorial in the May 1946 issue of the ANALYTICAL EDITION of INDUSTRIAL AND ENGINEERING CHEMISTRY. Space limitations prevent us from reprinting these comments in full, but one in particular needs to be repeated at frequent intervals.

No attempt is ever made to coerce any author into altering his manuscript against his wishes. Any compromise he makes as a result of reviewer suggestions is his own acknowledgment of sound criticism. Any revised draft he submits is assumed to be one that he, himself, approves, not one he has prepared to please the critics. If an author disagrees with reviewer criticisms, he is expected to inform the editors the reason or reasons for such disagreement, but he is under no obligation to make changes suggested by reviewers.

With the comments of both author and reviewers before him, it then becomes the duty of the editor and his associates to decide whether to accept or reject a manuscript—a responsibility not taken lightly. However, it is important for each author not to overlook the brief statement on the contents page of every ACS journal, which reads: "The AMERICAN CHEMICAL SOCIETY assumes no responsibility for the statements and opinions advanced by contributors to its publications."

Obviously, the primary purpose of the reviewing system is maintenance of high standards for ANALYTICAL CHEMISTRY. In most instances published manuscripts are improved as a result of the comments of reviewers. However, what appears in print is the responsibility of the author, and he cannot delegate this responsibility to others.

Trade-Mark Identification

TRADE-MARKS constitute valuable property and, as such, should be respected by authors when references are made to them in scientific and technical articles, and in news items.

If a trade-mark passes into the language as a generic term through the failure of the owner to protect it, it no longer is a valid trade-mark. This has happened not infrequently in the past, and it is understandable why owners of trade-marks seek the cooperation of editors in their efforts to prevent such losses.

The trade-mark laws prohibit the use of similar marks as trade-marks—that is, as a mark affixed by a person to his goods in order to identify and distinguish them from the goods of others. There is, however, no provision of law which prohibits the public from using trade-marks in a generic sense. The owner of a trade-mark must rely upon his advertising and upon the cooperation of publishers and editors, in order to avoid the loss of his trade-mark in this manner.

The editors of AMERICAN CHEMICAL SOCIETY publications wish to cooperate and have done so down through the years by capitalizing the first letter of a trade-mark. Just recently an informal poll of editors attending a meeting of the Society of Business Magazine Editors showed that the overwhelming majority of editors in that national organization followed this method of identifying trade-marks.

It is almost unnecessary for the editors of ACS publications to point out that Society journals contain a large proportion of papers reporting original research and, therefore, are referred to more frequently than other magazines serving the chemical field. Failure to identify a trade-mark in an ACS journal may compound this failure many times over.

ACS editors are conscientious in their efforts to identify trade-marks properly. Even so they need the help of authors and ask that authors make a serious effort to identify trade-marks in manuscripts submitted for publication. The editors also ask careful cooperation in the preparation of abstracts of papers for inclusion in the "Abstracts of Papers," issued by the ACS News Service prior to each national meeting.

Analytical Chemistry of the Less Familiar Elements

Papers presented at the Sixth Annual Summer Symposium sponsored by the Division of Analytical Chemistry and ANALYTICAL CHEMISTRY, Troy, N. Y., June 19 and 20, 1953

Analytical Chemistry of Beryllium

FRANK A. VINCI

The Brush Beryllium Co., 4301 Perkins Ave., Cleveland 3, Ohio

The analytical chemistry of beryllium is reviewed. Beryllium may be detected by a quick spot test utilizing *p*-nitrobenzeneazoörcinol; other color and fluorescence methods are available. Methods of separation are dealt with. A frequently used gravimetric method for the quantitative determination of beryllium employs the separation of beryllium hydroxide and ignition to oxide. Precipitation of ammonium beryllium phosphate, ignition, and weighing as beryllium pyrophosphate are also utilized. An empirical titrimetric method depends upon converting beryllium hydroxide to weakly ionized beryllium fluoride with consequent release of an equivalent quantity of alkali. A photometric procedure is based upon a nearly specific colored lake formation with *p*-nitrobenzeneazoörcinol in the presence of a sequestering agent which acts to remove interferences. Analytical procedures employed in the determination of the impurities usually present in beryllium metal are tabulated. Methods used in the analysis of ores and alloys of beryllium are summarized. Possible toxicological effects and means of guarding against them are pointed out.

BERYLLIUM and beryllium compounds (*21*) possess a generous supply of unique chemical and physical properties, which have won for this element increasing applications and widespread interest. As the use and availability of beryllium increase, more and more chemists are being confronted with analytical problems involving beryllium. Because information on the analytical chemistry of beryllium is generally scattered and somewhat controversial, this brief but orientative review of the available analytical methods has been undertaken.

At the present time beryl ($3BeO.Al_2O_3.6SiO_2$) is the only mineral of beryllium of commercial importance. Gem-beryl (emerald or aquamarine) approaches the theoretical composition of 14% BeO, 19% Al_2O_3, and 67% SiO_2 by weight, but commercial ore is contaminated with more or less quartz, feldspar, granite, and mica, with which it is usually associated as in pegmatite dikes.

Vauquelin (*48*) discovered the element in 1797. The metal itself was first produced by Wöhler (*56*) (and simultaneously and independently by Bussy) in 1828. By 1897 Lebeau (*24*) had produced a beryllium-copper alloy which was to give beryllium its first industrial foothold.

Beryllium is the only stable light metal with a high melting point (1285° C.). It possesses fair strength and good electrical conductivity, but generally poor ductility. It is extremely transparent to x-rays (thus is used for x-ray windows). It has low neutron capture and high neutron scatter cross sections and provides a good source of neutrons (thus is applicable as a moderator or reflector in nuclear power reactors).

Beryllium-copper alloys (*40*) are well known for their controllable precipitation hardening characteristics, unusual resistance to fatigue and impact, and nonmagnetic antisparking properties (thus they are used in precision instrument springs, diaphragms, circuit breaker parts, and gears).

Beryllium oxide is especially useful in refractory crucibles because of its high melting point, high thermal with very low electrical conductivity, and good resistance to thermal shock (*31*).

DISSOLUTION OF SAMPLE

For analytical purposes, beryllium metal is conveniently dissolved in diluted sulfuric acid. It is, however, readily attacked by all the commonly used mineral acids except nitric, which, if cold and concentrated, has little effect. Alkalies react with beryllium with the evolution of hydrogen. The hydroxide, $Be(OH)_2$, is amphoteric, and with excess alkali it forms beryllate. This differs from the corresponding aluminate in that the former is fairly easily hydrolyzed by heating or diluting its solution.

Beryllium oxide is practically insoluble in dilute hydrochloric acid, but it can be put into solution either by boiling with sulfuric and hydrofluoric acids or by fusion with potassium bisulfate.

Alloys of beryllium with copper, nickel, or cobalt are usually attacked with nitric acid; those with iron, aluminum, or magnesium are attacked with hydrochloric acid.

Powdered beryl ores respond best either to fusion (*32*) with sodium carbonate or to digestion with combined hydrofluoric and sulfuric acids.

DETECTION

In the general qualitative scheme of analysis, the sample solution, previously freed of silica and the members of the acid sulfide group, then boiled to expel hydrogen sulfide, is treated with ammonium hydroxide to a pH of 8.5. The precipitated combined hydroxides, including beryllium, aluminum, iron, and chromium,

are dissolved in acetic acid. The resulting solution is treated by the 8-quinolinol method to remove quinolates, which are insoluble in acetic acid–acetate buffered solution at a pH of 5.7. The filtrate is brought to a pH of 8.5 with ammonium hydroxide, boiled, and filtered. A white gelatinous precipitate caught on the filter paper is beryllium hydroxide and should be confirmed.

The *p*-nitrobenzeneazoorcinol spot test for beryllium (*23*) is a suitable test.

Spot Test. When a solution of *p*-nitrobenzeneazoörcinol (called Zenia) in 0.1 *N* sodium hydroxide is added to a moderately alkaline solution of beryllium, it turns immediately from yellow to red. This color change is the result of a selective colored lake formation (*14*).

To prepare the dye solution, dissolve 0.03 gram of *p*-nitrobenzeneazoörcinol powder (Eastman Kodak) in 100 ml. of 0.1 *N* sodium hydroxide solution by stirring with a mechanical stirrer for about 5 hours. Filter and store in a red (low actinic) glass bottle. Renew about once each month.

A portion (estimated to represent 1 to 10 mg. of beryllium) of the hydroxide precipitate, obtained by the general analytical procedure, is dissolved in 10 ml. of cold 2 *N* sodium hydroxide solution to give the test solution. Two drops of the dye solution are placed on a double thickness of filter paper, forming a brownish-yellow spot. One drop of the test solution is transferred to the center of the dye spot. A red to pink coloration confirms the presence of beryllium.

The following additional tests have been recommended for both detection (*53*) and quantitative estimation of beryllium:

1. Quinalizarin, 1,2,5,8-tetrahydroxyanthraquinone (*15, 43*).
2. Curcumin (*22*).
3. Alkanin or naphthazarin (*47*).
4. Naphthacrome Green G or Naphthachrome Azurine 2 B (*2*).
5. Aluminon (*25*).
6. Quinizarin, 2-sulfonic acid (*11*).
7. Morin, 3,5,7,2′,4′-pentahydroxyflavone (*39*).
8. Quinizarin, 1,4-dihydroxyanthraquinone (*16*).
9. 1-Amino-4-hydroxyanthraquinone (*55*).

The latter three tests depend upon fluorescence when an alkaline solution of beryllium is exposed to ultraviolet light. Compared to the *p*-nitrobenzeneazoörcinol test, some of the above listed tests are more sensitive, but all suffer from considerably greater interferences. This necessitates more complete isolation of beryllium preceding their application.

SEPARATIONS

Elimination of interfering quantities of other elements is often a prerequisite in the quantitative estimation of beryllium content. The following most frequently encountered methods of separation are suggested.

Removal of Phosphoric Acid. Phosphates are removed (in the usual manner) with ammonium molybdate from a solution made acid with nitric acid.

Separation of Beryllium from a Preponderance of Aluminum. Aluminum chloride is precipitated by the method of Gooch and Havens (*42*) from a concentrated solution of hydrochloric acid and ether saturated with hydrogen chloride gas. The small amounts of aluminum remaining can then be removed (if required) by means of the 8-quinolinol separation (*18*).

From a Preponderance of Iron. Ferric chloride can be extracted by ether from a cold hydrochloric acid solution having a specific gravity of 1.10. Alternatively, the acid solution treated with tartaric acid is rendered ammoniacal and saturated with hydrogen sulfide to precipitate the iron as sulfide.

From a Preponderance of Copper. If the determination of copper is not required, it is usually expedient to remove it as soluble tetramine copper complex. Sufficient ammonium hydroxide is added to convert all of the copper to the soluble blue complex, and the beryllium hydroxide formed is separated by filtration. To effect complete elimination of the copper, a double or triple precipitation may be required.

If the determination of the copper is required, electrodeposition on a platinum cathode from a solution made acid with nitric and sulfuric acids is most convenient, leaving a copper-free solution containing all the beryllium.

From a Preponderance of Nickel or Cobalt. Ammonium hydroxide added in excess permits complete precipitation of beryllium hydroxide, leaving the nickel and cobalt in solution in a manner analogous to removal of copper.

Separations by 8-Quinolinol (*3*). Beryllium is not precipitated as an insoluble quinolate from an acetic acid–acetate buffered solution at a pH of 5.7. All the other members of the ammonium hydroxide group are precipitated, with the exception of some of the rare earths and chromium, which may be incompletely precipitated. In addition, the separation serves to remove molybdenum, tungsten, uranium, copper, nickel, cobalt, zinc, cadmium, mercury, and bismuth, as well as more or less manganese and vanadium.

Separations by Mercury Cathode Electrolysis (*26*). Iron, chromium, nickel, cobalt, copper, tin, molybdenum, zinc, and lead can be removed from a solution weakly acid with sulfuric acid, leaving all the beryllium in solution.

Separations from Elements Forming Insoluble Phosphates in Fairly Strong Acid Solution. Zirconium, hafnium, and titanium can be precipitated with monoammonium phosphate from an acid solution containing 10% of either free concentrated sulfuric or hydrochloric acid solution by volume.

Separations by Cupferron. Iron, titanium, zirconium, hafnium, vanadium, tantalum, niobium, and quadrivalent uranium can be precipitated from an ice-cold solution containing free hydrochloric or sulfuric acid (but no oxidizing agents) by means of a 6% solution of cupferron.

Separation of Beryllium from Rare Earths. Elements of atomic numbers 58 to 71 and yttrium, plus scandium, actinium, and thorium can be removed as insoluble fluorides from a solution made acid with hydrofluoric acid.

Complexing with Salts of Ethylenediaminetetraacetic Acid. The use of the sodium salts of ethylenediaminetetraacetic acid as sequestering agents can occasionally eliminate the need for some of the above separations. For example, application of the disodium salt of ethylenediaminetetraacetic acid to the gravimetric determination of beryllium as the pyrophosphate and the tetrasodium salt to the photometric determination of beryllium are described below. Further applications are currently being investigated.

QUANTITATIVE DETERMINATION OF BERYLLIUM

The methods most widely used for the quantitative determination of beryllium include:

1. The gravimetric methods, used when accuracy takes precedence over speed and ease of analysis.
   a. Precipitation of beryllium hydroxide and ignition to BeO.
   b. Separation of beryllium ammonium phosphate and ignition to $Be_2P_2O_7$.
2. The volumetric "empirical titrimetric" procedure is applied when beryllium is the major constituent, the aluminum content is known and small, and interfering elements are absent.
3. The photometric *p*-nitrobenzeneazoörcinol method is used for the estimation of milligram or microgram quantities of beryllium.

After this article was prepared, the author's attention was called to a German work on the analytical chemistry of beryllium by Fresenius and Jander (*17a*), which discusses the gravimetric determination as hydroxide, sulfate, and phosphate; acidimetric and iodometric volumetric determination; colorimetric determination using quinalizarin and curcumin; determination of beryllium in minerals and alloys; and polarographic and spectrochemical determinations. Methods of separation from aluminum, iron, and other metals are given in detail.

Precipitation of Beryllium Hydroxide and Ignition to Beryllium

Oxide. This method, although widely used, contains many pitfalls. With the proper recognition of and the careful precaution against these pitfalls, it is capable of highly accurate results.

The solution from which beryllium hydroxide is to be finally precipitated must be free from all other members of the ammonium hydroxide group. The prepared solution is generally obtained, after prior removal of previous groups and citrates,

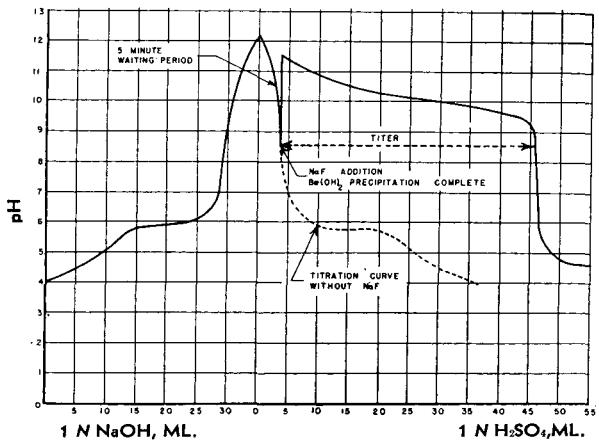


Figure 1. Potentiometric Titration Curve

For 0.2 gram of beryllium as beryllium sulfate treated by empirical titrimetric procedure

carbonates, fluorides, and phosphates, by precipitating the group members (beryllium, aluminum, gallium, indium, chromium, iron, selenium, actinium, titanium, zirconium, hafnium, thorium, niobium, tantalum, protactinium, and uranium plus the 16 rare earth elements of atomic numbers 58 to 71 inclusive, and yttrium) with freshly prepared ammonium hydroxide in the presence of ammonia salts at a pH of 8.5, and then removing all of these but none of the beryllium (see methods of separation).

The beryllium hydroxide finally reprecipitated is dried and then slowly decomposed to oxide at temperatures gradually rising to 700° C. (appreciable losses of beryllium oxide occur when it is heated at temperatures in excess of 700° C. in the presence of moisture) (*20*). The beryllium oxide is then ignited only once at 1100° C. for a minimum of 1 hour, cooled in a desiccator (preferably over anhydrous magnesium perchlorate), and quickly weighed as "impure" BeO. This always contains slight amounts of silica picked up from the glassware and reagents and may contain alumina. Oxides of other metals may also be present, owing to incomplete prior removal. All of these should be determined and their combined weights deducted from that of the impure beryllium oxide.

$$\text{Wt. of Be} = \text{wt. of BeO} \times 0.3603$$

Phosphate Method in Presence of Chelating Agent. Precipitation of beryllium ammonium phosphate with subsequent ignition to beryllium pyrophosphate has the advantage of giving almost four times as much mass to weigh per equivalent beryllium content as the beryllium oxide method. Prior removal of phosphates is not required, and the precipitate being somewhat granular, occlusion of impurities is less troublesome. If the conditions of precipitation are not meticulously controlled, slight departures from constant theoretical beryllium pyrophosphate composition may occur, resulting in loss of accuracy.

By taking advantage of the selective-order sequestering power of the disodium salt of ethylenediaminetetraacetic acid (*29*), arduous complete removal of many metal ions from the solution, prior to the precipitation of beryllium ammonium phosphate, can be omitted (*34*). If the amount of these metal ions, like magnesium, calcium, iron, aluminum, copper, and nickel, is roughly known, a slight excess of the chelating agent can be added to remove their interference. Beryllium (being only slightly sequestered at a pH of 5 to 5.5 by this excess) can then be precipitated with very little loss.

The hydroxides, containing from 1 to 10 mg. of beryllium, are precipitated at a pH of 8.5 with ammonium hydroxide, filtered, and dissolved back into the original beaker with dilute sulfuric acid. The solution is diluted to 100 ml. and adjusted to pH 2. Five milliliters of 15% diammonium phosphate solution and a slight excess of 15% disodium salt of ethylenediaminetetraacetic acid solution (both solutions previously adjusted to a pH of 5.5) are added. Ammonium acetate solution is added to a pH of 5.5. The solution is simmered at just below boiling for 5 to 10 minutes and cooled in a water bath for 0.5 hour. The granular precipitate is filtered, redissolved, and reprecipitated by using only 1 ml. of each of the two reagents. Final weighing after ignition at 1000° C. is as $Be_2P_2O_7$ (*1*).

$$\text{Wt. of Be} = \text{wt. of } Be_2P_2O_7 \times 0.0939$$

VOLUMETRIC DETERMINATION OF BERYLLIUM BY EMPIRICAL TITRIMETRIC METHOD

Beryllium can be completely precipitated as hydroxide from its sulfuric (or hydrochloric) acid solution at pH 8.5. If an excess of sodium fluoride is then added, the beryllium hydroxide is converted to very weakly ionized beryllium fluoride, liberating the hydroxyl ions as sodium hydroxide:

$$BeSO_4 + 2NaOH \xrightarrow[8.5]{\text{pH}} Be(OH)_2 + Na_2SO_4$$

$$Be(OH)_2 + 2NaF \longrightarrow BeF_2 + 2NaOH$$

This released alkalinity, determined by titration with standardized sulfuric acid solution, can be taken as a measure of the amount of beryllium present. Aluminum reacts in a similar

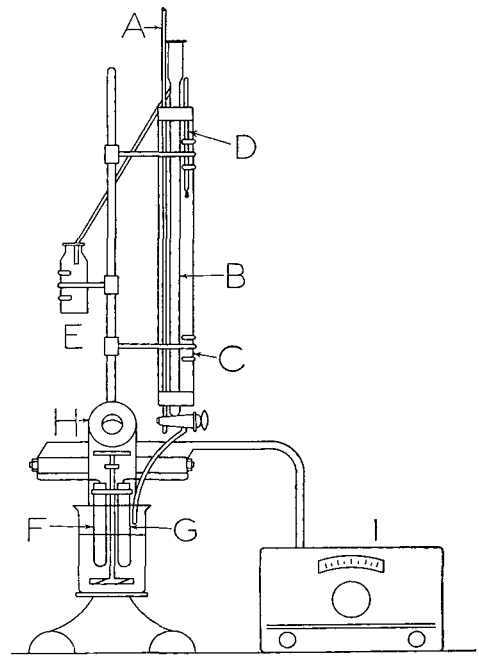


Figure 2. Potentiometric Titration Setup for Determination of Total Beryllium

A. 1 *N* sulfuric acid titrant from raised reservoir
B. Automatic bottom-fill 50-ml. buret
C. Water jacket around buret
D. Thermometer
E. Bottle for buret overflow
F. Reference calomel electrode
G. Glass electrode
H. Magic eye end-point indicator
I. Fisher Titrimeter control unit

manner; therefore it must be absent or corrected for if present. Zirconium, hafnium, rare earths, uranium, and thorium interfere and must be absent.

In practice, the above reaction does not seem to take place stoichiometrically, perhaps because of such complicating factors as the amphoteric character of beryllium. However, if the conditions of the titration are closely duplicated, the method, although empirical (*27*), becomes very useful because of its accuracy and relative speed. The titration must be performed precisely and slowly, giving sufficient time for the reactions to come to equilibrium. The 1 *N* titrating acid is standardized in terms of beryllium equivalent by using a portion of the acid solution to titrate the alkalinity released from an aliquot portion of standard beryllium sulfate solution (of gravimetrically predetermined beryllium content).

Figure 1 shows the potentiometric titration curve obtained when 0.2 gram of beryllium as beryllium sulfate is treated by the empirical titrimetric procedure. Figure 2 is a schematic diagram of the equipment used in obtaining the curve.

PHOTOMETRIC DETERMINATION OF BERYLLIUM

When a solution of *p*-nitrobenzeneazoorcinol (*33*, *46*) in 0.1 *N* sodium hydroxide is added to a moderately alkaline solution containing beryllium, a red-brown lake results. The absorption of light by this colored complex does not strictly follow Beer's law, but by careful control and duplication of conditions such as optimum alkalinity, amount of foreign ions, dye strength, and temperature, the relationship of light absorption to beryllium content can be accurately fixed. This provides a photometric method for the estimation of beryllium content.

Correct alkalinity, the range of which is small and critical, is maintained by means of a sodium borate–citrate buffer. The dye is nearly specific for beryllium, reacting in an interfering manner only with magnesium and to a much smaller extent with zinc. Metals like copper, nickel, iron, and calcium which form colored ions or precipitates in the alkaline solution, as well as zinc and magnesium, are rendered inactive through formation of soluble nonionic chelates if present in limited amounts.

Table I. Analysis of Beryllium Metal

Determination	Average Analysis, P.P.M.	Method of Determination
1. Total Be	99.1%	Volumetric, empirical titrimetric
2. Total Fe	1350	Photometric, thiocyanate or *o*-phenanthroline
3. Total Al	300	Fluorimetric, Pontochrome Blue-Black R; Gravimetric; or colorimetric Al-quinolate
4. Total Mn	150	Photometric, permanganate, persulfate oxidation
5. Total Cr	100	Photometric, diphenylcarbazide, periodate oxidation
6. Total Ni	200	Photometric, dimethylglyoxime
7. Total Cu	100	Photometric, dithizone
8. Total Mg	80	Gravimetric, pyrophosphate
9. Total Si	600	Photometric, molybdenum blue
10. B	0.5	Methyl borate distillation and turmeric colorimetric
11. BeO	0.80%	Dry HCl gas evolution, followed by *p*-nitrobenzeneazoörcinol colorimetric
12. Be_2C	0.14%	Evolution of methane and ignition to CO_2
13. Be_3N_2	0.02%	Micro-Kjeldahl
14. H_2O	0.15%	H_2 evolution and ignition to H_2O
15. Ag	3	Polarographic or spectrographic
16. Co	3	Polarographic or spectrographic
17. Cd	0.2	Polarographic or spectrographic
18. Pb	30	Polarographic or spectrographic
19. Zn	30	Polarographic or spectrographic
20. Li	0.3	Spectrographic or by flame photometry
21. Ca	40	Spectrographic

Reagents. Standard Beryllium Solution. Using beryllium metal powder of known assay and dissolving by means of 20 ml. of 1 to 1 sulfuric acid per gram of metal, a solution to contain 0.072 mg. of beryllium in 1 ml. is made up.

Buffer Solution. Sodium citrate dihydrate (17.8 grams), 8.5 grams of sodium borate pentahydrate, and 14.35 grams of sodium hydroxide are dissolved in water and made up to 100 ml.

Zenia Dye Solution. *p*-Nitrobenzeneazoörcinol powder (Eastman Kodak, 0.075 gram) is dissolved in 250 ml. of 0.1 *N* sodium hydroxide solution by stirring with a mechanical stirrer for 5 hours, filtered through an asbestos mat, and stored in a red (low actinic) glass bottle.

Versene T Solution, 13.9%. A 55.5% water solution of Versene T [a blend of tetrasodiumethylenediaminetetraacetate and triethanolamine available from the Bersworth Chemical Co. (*6*)] is diluted 1 volume with 3 volumes of distilled water.

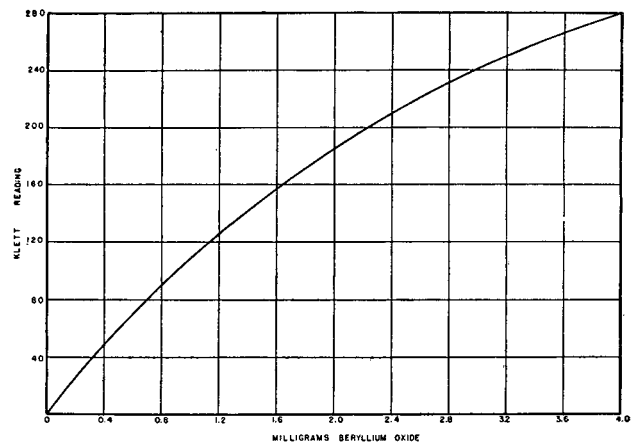


Figure 3. Photometric *p*-Nitrobenzeneazoörcinol Method for Estimation of Beryllium Content

Sample calibration curve

Procedure. The cooled sample solution containing from 0.06 to 1.1 mg. of beryllium and no more than 5 mg. of magnesium, 20 mg. of calcium, 10 mg. of iron, or 35 mg. of aluminum is adjusted to a volume of 35 ml. Five milliliters of Versene T solution are added and the pH is adjusted to 5.5. After 5 minutes, 10 ml. of buffer solution are added. Five minutes later, exactly 10 ml. of *p*-nitrobenzeneazoorcinol solution are added. The solution is made up to 100 ml., mixed, and allowed to stand 10 minutes. The transmittancy is finally determined with the spectrophotometer adjusted to 100% transmittance with a reagent blank. A 515-mμ wave length and a 20-mm. light path cuvette are employed. The milligrams of beryllium present are determined from a previously constructed calibration curve. Figure 3 shows a sample calibration curve obtained with a Klett-Summerson photoelectric colorimeter utilizing a green (No. 54) filter and a 20-mm. light path cuvette.

ANALYSIS OF BERYLLIUM METAL

Table I serves to summarize a typical chemical analysis of an average sample hot pressed from powder beryllium metal and to indicate the method of determination (*3*, *9*, *13*, *30*, *35–38*, *44*, *49*, *51*, *54*).

Determinations 1 to 8 are performed on individual aliquots of a single sulfuric acid solution of the sample. Determinations 9 to 14 are performed on individual portions of metal sample. Determinations 2 to 9 and 15 to 21 can be performed spectrographically. Determinations 1 and 10 to 14 are performed only by wet chemical methods. Determination 14 refers only to beryllium metal powders.

Of these methods, the beryllium oxide and beryllium carbide procedures are unusual and need further description.

Determination of Beryllium Oxide in Beryllium Metal. The determination of beryllium oxide in beryllium metal is based upon the fact that at temperatures of 520° to 800° C. dry hydrogen chloride gas will, when passed over beryllium metal, convert it to beryllium chloride, which is volatilized off:

$$Be + 2HCl \xrightarrow[800^\circ\ C.]{} BeCl_2 + H_2$$

The beryllium contents of both beryllium carbide and beryllium nitride are also volatilized off as beryllium chloride:

$$Be_2C + 4HCl \longrightarrow 2BeCl_2 + CH_4$$

$$Be_3N_2 + 8HCl \longrightarrow 3BeCl_2 + 2NH_4Cl$$

The beryllium oxide content is unattacked and remains as a residue in the boat. It can be put into solution and the quantity present ascertained by the photometric method.

Figure 4 shows the equipment used in carrying out the above determination.

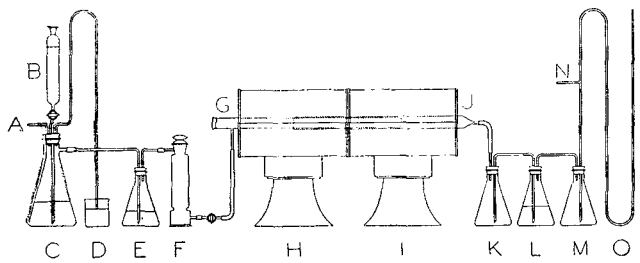


Figure 4. Apparatus for Determination of Beryllium Oxide Content in Beryllium Metal by Dry Hydrogen Chloride Gas Evolution Method

A. Helium gas inlet
B. 250-ml. separatory funnel filled with hydrochloric acid
C. 2-liter filter flask half filled with concentrated sulfuric acid
D. 30-inch mercury manometer and reservoir
E. 500-ml. flask partially filled with concentrated sulfuric acid
F. Drying tower filled with anhydrous magnesium perchlorate
G. Clear quartz tube, 7/8 inch in outside diameter and 22 inches long, with side arm near open end and orifice 3/16 inch in diameter at opposite end
H. Hevi-duty tube furnace, temperature varied from 600° to 800° C.
I. Hevi-duty tube furnace maintained at 900° to 1000° C.
J. Fused quartz tube, 1.25 inches in outside diameter, 1 inch in inside diameter, 30 inches long, reduced end
K, L, M. 500-ml. flasks. *L* contains concentrated sulfuric acid
N. To water aspirator
O. Water manometer

Determination of Beryllium Carbide in Beryllium Metal. This method is based upon the fact that beryllium carbide is attacked by hot 60% potassium hydroxide solution, liberating methane:

$$Be_2C + 4KOH \rightarrow 2K_2BeO_2 + CH_4$$

Simultaneously the beryllium metal is dissolved and hydrogen is evolved:

$$Be + 2KOH \rightarrow K_2BeO_2 + H_2$$

The evolved methane and hydrogen can be oxidized to carbon dioxide and water by passing over copper oxide wire (packed in a quartz tube) heated to 600° to 800° C.

$$H_2 + CuO \rightarrow Cu + H_2O$$

$$CH_4 + 4CuO \rightarrow 4Cu + 2H_2O + CO_2$$

All the water formed (*5*) can be removed by absorption in anhydrous magnesium perchlorate. The carbon dioxide is then absorbed in Ascarite and weighed in the usual manner

Figure 5 shows the apparatus used.

ANALYSIS OF ORES AND OXIDES OF BERYLLIUM

Ores of Beryllium (*8, 10, 17, 19, 50*). Following dissolution of the sample and volatilization of its silica content, the ammonium hydroxide group is precipitated, filtered, and redissolved in acid. If an average error of ±5% of the beryllium content present is acceptable, the colorimetric procedure is employed. The method is fairly rapid, specific, and applicable to rich or low grade ores alike. In the case of low grade ores, however, excesses of aluminum and iron must be removed. Alternatively, the much lengthier gravimetric determinations by finally weighing as beryllium oxide or beryllium pyrophosphate are generally employed where higher accuracy is demanded. These are recommended only in the case of beryl ores containing more than 1% beryllium oxide.

Alloys of Beryllium (*50*). Beryllium-copper alloys are the most industrially important alloys of beryllium. These include Master-alloy containing 4 to 4.25% beryllium with about 0.1% iron, 0.06% aluminum, and 0.08% silicon as impurities and the ternary alloys employing nickel or cobalt hardener and made from the Master-alloy. The most common of these contain about 2% beryllium with 0.35% nickel or cobalt and 0.25% beryllium with 2% nickel or cobalt.

The beryllium in the above alloys can be determined by any of the methods given. When the spectrophotometric procedure is used, the size of sample should be chosen to contain about 0.3 mg. of beryllium. However, at least 1 gram of the metal sample should be dissolved. Where necessary, an appropriate aliquot of the acid solution of the combined hydroxides can be taken to provide the proper quantity of beryllium for the determination. The volumetric procedure is capable of much better accuracy than the photometric method, provided that the size of the sample is large enough to contain 0.1 to 0.2 gram of beryllium and that the aluminum content is known and small. This procedure is expediently used when the copper is first removed by electrodeposition.

DETERMINATION OF BERYLLIUM CONCENTRATION IN ATMOSPHERE

It has been recognized for some time that exposure to an atmosphere contaminated with beryllium or its compounds may, under certain conditions and in ways not yet fully understood, give rise to health hazards (*4, 7, 12, 28, 41, 45, 52*). Toxicologic reactions involving either the derma or the respiratory tract may occur.

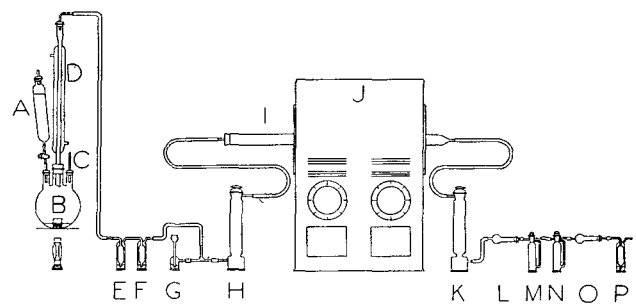


Figure 5. Train Setup for Determination of Beryllium Carbide by Methane Evolution

A. 150-ml. separatory funnel containing 100 ml. of potassium hydroxide solution
B. 500-ml. 3-necked borosilicate distillation flask
C. Nitrogen inlet
D. Water-cooled condenser
E, F. Bubblers containing concentrated sulfuric acid
G. Mercury safety manometer
H. Drying tower filled with Ascarite
I. Fused quartz tube, 1.25 inches in outside diameter, 1 inch in inside diameter, 30 inches long, reduced end
J. Lindberg Glo-bar combustion furnace
K. Drying tower filled with anhydrous magnesium perchlorate
L. Drying tube filled with Drierite
M. Nesbitt weighing bulb packed with Ascarite and bottom layer of Drierite
N. Nesbitt counterpoise bulb, packed like *M*
O. Drying tube filled with anhydrous magnesium perchlorate
P. Bubbler containing concentrated sulfuric acid

The analyst, as well as other workers handling products containing beryllium, should conduct all dust-, fume-, or vapor-producing operations in a well ventilated hood. Whenever excessive dusting or fuming is involved, the hood should be exhausted through proper equipment (electrostatic precipitator, filter, or scrubbing tower) to remove the beryllium from the air.

In 1950 the United States Atomic Energy Commission recommended the following tentative maximum exposure levels (*7*): 2 γ

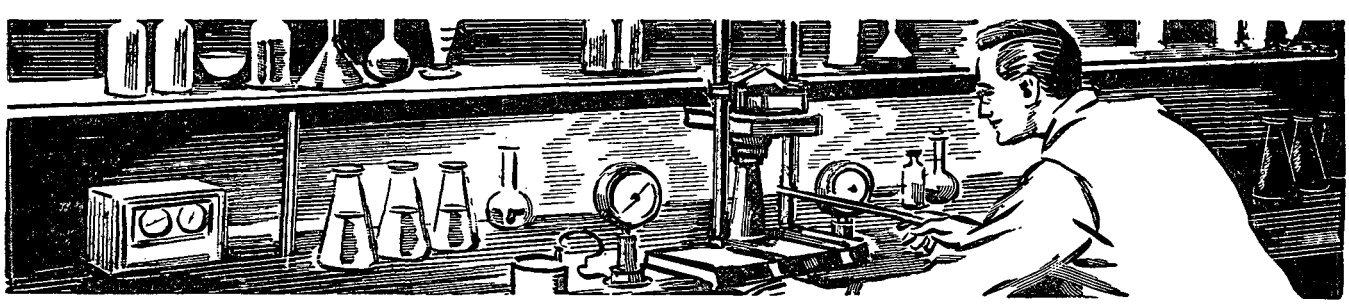
of beryllium per cubic meter average concentration throughout an 8-hour day; 25 γ per cubic meter in a single exposure; and 0.01 γ per cubic meter average monthly concentration at breathing zone levels in outside surrounding areas.

To evaluate the degree of beryllium concentration in an atmosphere possibly contaminated with beryllium, a measured volume of air is drawn through a filter. The filter pad with the beryllium-bearing dust or fume collected upon it is analyzed for its beryllium content by spectrographic, fluorometric (*52*), or photometric (*41*) methods following appropriate treatment to destroy the organic matter of the filter and to remove interfering quantities of other elements.

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Spectrophotometric Determination of Selenium and Tellurium in Concentrated Sulfuric Acid

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The need for determining small amounts of tellurium in magnesium alloys led to the development of a spectrophotometric method. Selenium was included in the investigation because of its similar chemical nature. Tellurium or selenium is precipitated from solution by reduction, and dissolved in concentrated sulfuric acid. The absorbance of the solution is measured at 350 mμ for selenium and at 520 mμ for tellurium. Using a 1-cm. cell, 50 γ of tellurium or 200 γ of selenium per 50 ml. of sulfuric acid solution can be determined. Tellurium in magnesium alloys has been successfully determined by this method. Selenium can be determined in the presence of equal amounts of tellurium, but tellurium cannot be determined in the presence of equal amounts of selenium.

A QUANTITATIVE colorimetric method for the determination of small quantities of tellurium and possibly selenium was desired for the analysis of magnesium alloys. Feigl (*3*) has reported a qualitative method for the detection of selenium or tellurium based on the color of these elements in concentrated sulfuric acid. According to Feigl, a green or red solution results because of the formation of loose addition compounds between selenium or tellurium and the anhydride of sulfuric acid according to the following equations

$$Se + H_2SO_4 \rightarrow Se.SO_3 + H_2O$$

$$Te + H_2SO_4 \rightarrow Te.SO_3 + H_2O$$

These compounds are decomposed into their components by water, and red selenium or black tellurium precipitates. Boitsova and Butkov (*2*) measured the absorption spectrum of tellurium dissolved in concentrated sulfuric acid with a quartz spectrograph. They reported an absorption maximum at 5180 A. and a minimum at 3960 A. Moles (*5*) made cryoscopic measurements on solutions of selenium and tellurium in concentrated and fuming sulfuric acid. The molecular weights he obtained varied considerably with the type of acid used. He believed the complex of selenium to be $SeSO_3$ or a polymer $(SeSO_3)_x$. Moles also reported that the solubility of selenium in concentrated sulfuric acid is greater for the red amorphous variety than for the gray metallic selenium. Auerbach (*1*) reported, however, that "metallic" selenium dissolves in fuming sulfuric acid as Se and tellurium as Te.

To the authors' knowledge no mention has been made in the literature of the quantitative determination of selenium and tellurium based on the color of their complexes in concentrated sulfuric acid. This investigation was undertaken to see whether such an approach was feasible.

REAGENTS AND EQUIPMENT

Selenium (red powder of estimated purity better than 99.9%), obtained from Eimer and Amend.

Tellurium (estimated purity better than 99.0%), obtained from the Raritan Copper Works. To obtain powdered tellurium, flakes of the tellurium are dissolved in 6*N* nitric acid. The solution is evaporated to a small volume and then diluted with 3*N* hydrochloric acid. The tellurium is precipitated as a finely divided solid with sulfur dioxide, washed with water followed by alcohol, and then dried at 100° C.

Sulfuric acid (98%), reagent grade

Sulfurous acid (6% sulfur dioxide minimum), reagent grade

Stannous chloride solution, 115 grams of stannous chloride dissolved in 170 ml. of 12*N* hydrochloric acid. The resulting solution is diluted to 1 liter and stored over tin.

Beckman Model B spectrophotometer. All measurements are made in 1-cm. cells.

PROCEDURE

Selenium. Concentrated sulfuric acid at a temperature of 175° ± 5° C. is added to the selenium in a 150-ml. beaker. The solution is maintained at 175° C. for 15 minutes, and then allowed to cool. After the solution has been transferred to a 50- or 100-ml. borosilicate glass volumetric flask and diluted to the mark with concentrated sulfuric acid, the absorbance is measured at 350 mμ with a suitable spectrophotometer.

Tellurium. The tellurium is dissolved by a procedure similar to that described for the selenium, except that the temperature of the sulfuric acid should be 100° ± 5° C., the time of heating should be 10 minutes, and the absorbance should be measured at 520 mμ.

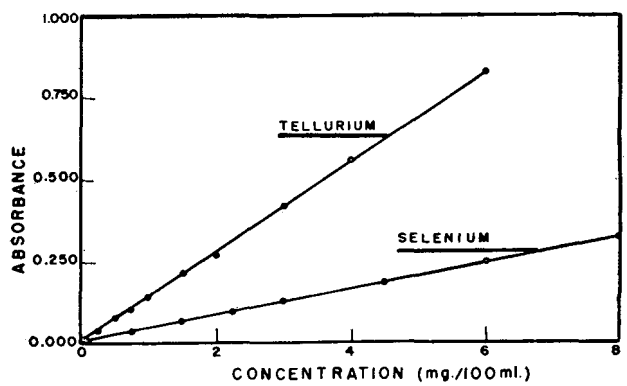


Figure 1. Calibration Curves for Determination of Selenium and Tellurium

Calibration Curves. Stock solutions containing known amounts of selenium and tellurium were prepared according to the procedures just described. Suitable aliquots of these stock solutions were added to 50- or 100-ml. borosilicate glass volumetric flasks and diluted to the mark with concentrated sulfuric

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[2] Present address, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.

acid. The absorbancies of these solutions were measured against concentrated sulfuric acid in the reference cell and plotted against the concentration.

Typical calibration curves for selenium and tellurium are shown in Figure 1. The straight-line relationship between absorbance and concentration shows that these solutions obey Beer's law.

Analysis of Samples. A sample of the unknown material containing from 2 to 10 mg. of selenium or 0.5 to 4 mg. of tellurium is dissolved with heating in 25 ml. (or more if necessary) of 3*N* hydrochloric acid. Approximately 2 ml. of 6*N* nitric acid is then added to dissolve the selenium or tellurium.

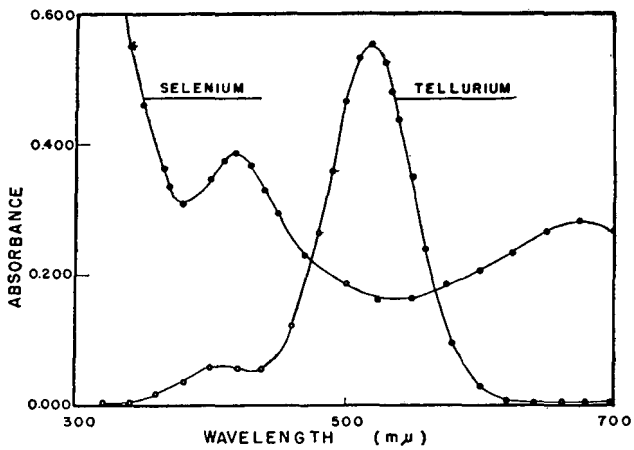


Figure 2. Absorption Spectra of Selenium and Tellurium in Concentrated Sulfuric Acid

The solution is evaporated to a small volume and then diluted again with 3*N* hydrochloric acid. The selenium or tellurium is then precipitated with 5 ml. of stannous chloride solution. The precipitate is filtered on a small sintered-glass filter funnel with suction, washed with water and finally with alcohol, and then dried at 100° C. Approximately 35 ml. of hot concentrated sulfuric acid is added to a small beaker containing the sintered-glass funnel. The temperature of the acid should be 175° C. for the selenium and 100° C. for the tellurium, and should be maintained for 15 minutes for the selenium and 10 minutes for the tellurium. After cooling, the solution is transferred to a 50-ml. volumetric flask and diluted to the mark with concentrated sulfuric acid. The absorbance of the solution is measured at 350 mμ for the selenium and at 520 mμ for the tellurium, and the concentration obtained from the standard calibration curve.

Three samples of magnesium alloys containing 5% zinc and small amounts of tellurium were analyzed by this procedure. For comparison, these samples were also analyzed by a standard gravimetric procedure (*4*) using sulfurous acid as the reducing agent. Three determinations were made on each sample and the precision is reported as the average deviation. The results are shown in Table I.

In every case slightly higher results were obtained by the colorimetric method. This may have been caused by incomplete precipitation of the tellurium in the gravimetric method, since the stannous chloride is a more efficient reducing agent than sulfurous acid. Stannous chloride was not used in the gravimetric procedure because it coprecipitates with the tellurium (*4*).

The colorimetric procedure required smaller samples (2 grams as compared to 15 grams) and yielded better precision (14 as compared to 30 parts per thousand).

DISCUSSION OF VARIABLES

Absorption Spectra. A solution containing 0.156 mg. of selenium per ml. of concentrated sulfuric acid was prepared according to the recommended procedure. The absorption spectrum was measured between 320 and 700 mμ. The results obtained are plotted in Figure 2. Although a slight peak occurs at 420 mμ, the wave length finally selected for measurement was 350 mμ. This wave length shows less interference from the tellurium and greater sensitivity than the one at 420 mμ. In addition, the peak at 420 mμ varies more critically with the time of heating and the temperature of the sulfuric acid used in dissolving the selenium. Values below 350 mμ are not satisfactory, as sulfuric acid begins to absorb.

Table I. Analysis of Magnesium Alloys

	Sample Number		
	485	486	487
	% Tellurium		
Colorimetric	0.134 ± 5 p.p.t.	0.093 ± 20 p.p.t.	0.096 ± 16 p.p.t.
Gravimetric	0.123 ± 30 p.p.t.	0.087 ± 35 p.p.t.	0.089 ± 28 p.p.t.

The absorption spectrum of a solution containing 0.04 mg. of tellurium per ml. of concentrated sulfuric acid was also determined from 320 to 700 mμ. The results are plotted in Figure 2 for comparison with the selenium. In the case of tellurium a sharp maximum occurs at 520 mμ, and this wave length was selected for measurement of the tellurium complex.

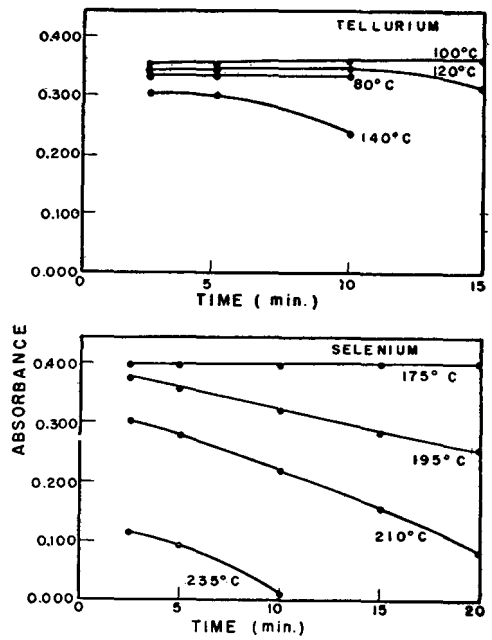


Figure 3. Effect of Temperature and Time of Heating on Absorbancies of Selenium and Tellurium Complexes

Temperature and Time of Heating. To determine the optimum temperature and the time of heating for the analysis of selenium, 10-mg. samples of selenium were treated with hot concentrated acid maintained at known temperatures for known periods of time. The temperature was varied between 100° and 235° C. and the time between 2.5 and 20 minutes. After cooling, the samples were diluted to 100 ml. in volumetric flasks. The results are shown in Figure 3. At temperatures below 175° C. the results were erratic, as the samples did not completely dissolve. Above 175° C. the samples dissolved completely but the colored complex was unstable and very dependent upon the time of heating. For these reasons, the temperature selected was 175° C. and the time of heating selected was 15 minutes.

A similar set of experiments was carried out for tellurium.

For the determination of tellurium the optimum temperature was 100° C. and the optimum time of heating was 10 minutes (See Figure 3).

Absorption of Water Vapor. Because sulfuric acid is a strong dehydrating agent, the effect of adding water to the selenium and tellurium complexes in concentrated sulfuric acid was studied. The amounts of water added varied from 0 to 10% of the total volume of the solution. In the case of selenium, the peak at 420 mμ disappears upon the addition of water. The absorbance at 350 or 375 mμ remains unchanged. With larger amounts of water, selenium precipitates.

In the case of tellurium the absorbance at 520 mμ decreases slightly upon the addition of water as the tellurium precipitates. In an analysis, if the volumetric flasks are kept stoppered, the absorption of water vapor will not cause noticeable errors.

Stability of Solutions. Both the selenium and tellurium complexes in concentrated sulfuric acid are very stable on standing. Over a period of 24 hours there is no change in absorbance, and after several weeks the change in absorbance is less than 10%.

Mixtures of Selenium and Tellurium. As there is such a wide difference in the temperatures necessary to dissolve the selenium and tellurium, several mixtures of approximately equal amounts of selenium and tellurium were prepared, and then analyzed by dissolving the mixture at either 175° or 100° C. In the mixtures analyzed for selenium by heating at a temperature of 175° C., the tellurium was converted to a colorless form, and the results for selenium were approximately 5% high.

In the case of the tellurium very erratic results were obtained on the mixtures dissolved at 100° C. Even at 100° C. some of the selenium dissolves and destroys the color of the tellurium complex. Apparently the rate of disappearance of the tellurium complex is dependent upon the amount of selenium present in the sulfuric acid solution.

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Determination of Impurities in Germanium and Silicon

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As a result of the current interest in the use of semiconductors in electronics it has been necessary to develop quantitative chemical methods for the determination of metal impurities in the semiconductor materials employed. Photometric methods have been developed for the determination of 0.1 to 1 p.p.m. of arsenic, phosphorus, antimony, and copper in germanium and germanium dioxide. In addition, a method for the determination of 1 to 10 p.p.m. of arsenic in silicon metal has been developed. The methods are designed to be used for quality control of raw materials and as an aid in research and manufacturing processes.

IN CONJUNCTION with the intensive research on semiconductors that is in progress in these laboratories it has been necessary to develop quantitative chemical methods for the determination of metal impurities in the semiconductor materials used. The authors' analytical program calls for the development of methods of analysis for the Group V metals (arsenic, antimony, and phosphorus), for the Group III metals (aluminum, gallium, indium, and boron), and for copper, in germanium dioxide and in germanium and silicon metal. To date, methods for the determination of 0.1 to 1 p.p.m. of arsenic, phosphorus, antimony, and copper in germanium and germanium dioxide have been completed. In addition, a method for the determination of 1 to 10 p.p.m. of arsenic in silicon metal has been developed.

In trace analysis it is usually necessary to isolate the impurity in question before attempting its determination. Fortunately, germanium can be easily removed by distillation as chloride without loss of most of the metal impurities mentioned. Arsenic and boron must be separated by other means.

In view of the small amounts of metal impurities present in the samples to be analyzed, very sensitive methods are required. Because spectrophotometry is one of the analyst's most sensitive tools, it appeared that this might be a good approach to the problem. This has proved to be true. By choosing the most sensitive photometric methods, by using as large a sample and as long a light path as possible, and by purifying reagents, extremely high sensitivity has been obtained. In order to keep the blank due to the glassware to the minimum, Vycor No. 7900 glassware was used wherever possible. A Beckman DU spectrophotometer with a tungsten lamp and 5-cm. Corex absorption cells was used in the photometric work.

In all the methods developed, precautions have been taken to prevent interference of other metals that may be encountered. In some instances this has necessitated the use of a number of separations and other operations. If any or all of the interfering metal ions can be shown to be absent, by qualitative spectrochemical analysis or by other means, it is obvious that the methods can be greatly simplified. The following metals were used in the specificity tests of the methods developed: aluminum, antimony, arsenic, barium, beryllium, bismuth, boron, cadmium, calcium, cerium, chromium, cobalt, copper, gallium, germanium, gold, hafnium, indium, iridium, iron, lanthanum, lead, lithium, magnesium, manganese, mercury, molybdenum, neodymium, nickel, niobium, osmium, palladium, phosphorus, platinum, potassium, rhenium, rhodium, ruthenium, samarium, scandium, selenium, silicon, silver, sodium, strontium, tantalum, tellurium, thallium, thorium, tin, titanium, tungsten, uranium, vanadium, yttrium, zinc, and zirconium.

Data obtained on the analysis of mixtures of very pure samples of germanium dioxide, germanium, or silicon, plus measured quantities of the impurities to be determined, show that the methods all yield satisfactory results. Recoveries of 1 to 10 γ of the metal impurity from 3 grams of germanium dioxide, 2 grams of germanium, or 0.5 gram of silicon were quantitative. The reagent blank was, in all cases, of the order of 0.2 to 0.4 γ of impurity and the blank on the reagents plus the pure germanium dioxide, germanium, or silicon was not significantly higher than that of the reagent blank alone.

DETERMINATION OF ARSENIC

In preliminary tests it was shown that a fairly good separation of traces of arsenic from large amounts of germanium could be obtained by removal of the germanium by distillation as chloride from hydrochloric acid solution containing a little nitric acid. However, because recoveries of arsenic were about 5% low and further separations would be required, this method was abandoned.

The method finally chosen for the determination of arsenic in germanium and germanium dioxide is a modification of one developed by Payne (*3*). His method consists of solution of the sample in oxalic acid plus hydrogen peroxide, isolation of the arsenic by the Strafford, Wyatt, and Kershaw (*5*) diethylammonium diethyldithiocarbamate–chloroform extraction from 2 *N* hydrochloric acid solution, and determination by a Gutzeit method. In the present investigation a photometric molybdenum blue method has been used in place of the Gutzeit method because of the difficulties associated with the latter method.

In the photometric method adopted, formation of the heteropoly complex and reduction to molybdenum blue are accomplished in 0.2 *N* hydrochloric acid solution. Under these conditions the method provides high sensitivity and, in addition, has the distinct advantage that interference due to silicon and germanium is relatively low.

In order to determine the specificity of the molybdenum blue method adopted for arsenic, the behavior of each of the 56 metals listed above has been investigated. Fifty-microgram portions of the metals in solution were used in the tests. The metal ion solutions used here and in other specificity tests described below were prepared by obtaining appropriate portions of pure metals, oxides, or salts in alkaline, neutral, or acid solution. The only acids used were hydrochloric or perchloric acids. Alkaline solutions were stored in polyethylene bottles. The results showed that phosphorus produces a color which is, on a molar basis, approximately equal to that produced by arsenic. Germanium and silicon produce colors whose intensities are only about $^1/_{10}$ or $^1/_{50}$, respectively, of that of arsenic on a weight basis. Zirconium causes very low results due to precipitation of arsenate. Tungsten, niobium, and tantalum cause the results for arsenic to be about 10% low, presumably because of formation of complex acids. Selenium and gold precipitate as metal.

In the method described, arsenic is separated from most of the germanium and from all the other interfering metals by a carbamate-chloroform extraction from hydrochloric-oxalic acid solution. Copper, bismuth, and mercury, if present, will accompany the arsenic but cause no interference in the photometric method, providing sufficient hydrazine sulfate is present to overcome the oxidizing action of the copper. In spite of the complexing action of the oxalic acid on the germanium during the carbamate extraction, the chloroform layer always becomes contaminated by traces of germanium salts. Because of this it is necessary to remove the chloroform by distillation, destroy the organic matter by oxidation with nitric and perchloric acids, and then remove the remaining germanium by distillation as chloride before the photometric determination of the arsenic. No loss of arsenic has been noted during the wet oxidation of the carbamate. Moreover, because of the limited time and temperature of the distillation with hydrochloric acid, no loss of arsenic occurs during the removal of the traces of germanium.

So far as the authors have investigated, the findings of Strafford, Wyatt, and Kershaw have been confirmed. The extraction of arsenic is incomplete if sodium diethyldithiocarbamate is used in place of the diethylammonium compound. Moreover, the addition of the sodium carbamate results in the momentary formation of a white precipitate that does not completely redissolve. When this happens, appreciable contamination of the chloroform layer with germanium salts occurs. Arsenic must be completely in the trivalent condition at the time of extraction. In order to prevent air oxidation, it is best to allow the arsenic to be reduced by standing 15 minutes in the funnel in which the extraction is to be made. Low results are obtained if the acidity is too low or if the solution is too hot at the time of reduction and extraction. When the reduction and extraction are properly done, complete separation of the arsenic with a single extraction is possible.

The arsenic method has been adapted to the analysis of silicon metal. In this method it is important to control the volume of solution and the acidity, so that formation of a gel is prevented. Traces of silicon that may accompany the arsenic into the chloroform layer are subsequently made harmless by dehydration with perchloric acid.

APPARATUS

Forged Tool Steel Plattner Mortar and Pestle. Not all commercially available Plattner mortars are satisfactory. It is essential that the one used in these analyses be sufficiently smooth and hard to keep contamination of the sample with iron to the minimum.

Platinum Sieve. A circular piece of 150-mesh platinum wire screen 2.5 inches in diameter, supported in a Plexiglas frame.

Squibb-Type Separatory Funnels. Squibb-type, pear-shaped, 150-ml. borosilicate glass separatory funnels with glass stoppers. The stem of each funnel should be cut off so that only about 1 cm. is left below the stopcock. The stopcock and stopper should fit snugly. When a stopcock begins to show signs of wear, the funnel should be discarded, as a leaky stopcock may prevent a clean separation of the arsenic and germanium. No lubricant should be used on the stopcocks or stoppers in this or subsequent methods described.

REAGENTS

Distilled Water. In order to obtain satisfactory results in the determination of small amounts of metal impurities, it is necessary to use very pure distilled water in the preparation of the reagents and in the analyses. In the development of the present method, as well as those described subsequently, ordinary distilled water was passed through a mixed cation-anion exchange resin mixture before use.

Chloroform. The chloroform used in this method and those described subsequently should be freed of contaminating metal ions by redistillation from an ordinary borosilicate glass still.

Perchloric Acid. The perchloric acid used in this and succeeding methods should contain 70 to 72% by weight of perchloric acid.

Standard Arsenic Solution (1 γ of Arsenic per Ml.). Transfer 0.0660 gram of NBS sample 83a, arsenious oxide, to a 100-ml. platinum dish and add 20 ml. of distilled water plus 1 pellet of sodium hydroxide. Cover and warm to dissolve the arsenious oxide completely. Cool, add 5 ml. of perchloric acid, transfer to a 500-ml. volumetric flask, dilute to the mark, and mix. Transfer 10.0 ml. of the solution to a 1-liter volumetric flask, add 10 ml. of perchloric acid, dilute to the mark, and mix.

Methyl Red Solution. Dissolve 0.020 gram of methyl red (sodium salt) in 100 ml. of distilled water.

Potassium Bromate Solution. Dissolve 0.030 gram of potassium bromate in 100 ml. of distilled water.

Ammonium Molybdate Solution. Dissolve 1.000 gram of large crystals of ammonium molybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$, in 50 ml. of distilled water in a 100-ml. volumetric flask, dilute to the mark, and mix. The solution must be clear. Do not filter through paper. Store in a polyethylene bottle. If a glass bottle is used, the solution tends to turn yellow as silica is dissolved, and high blanks for arsenic are obtained.

Hydrazine Sulfate Solution. Dissolve 0.160 gram of hydrazine sulfate, $(NH_2)_2.H_2SO_4$, in distilled water in a 100-ml. volumetric flask, dilute to the mark, and mix.

Diethylammonium Diethyldithiocarbamate Solution (DDC Solution). Dissolve 20 grams of Eastman's diethylammonium diethyldithiocarbamate in 250 ml. of ethyl ether by heating in a flask with an air-cooled reflux condenser. Add some carbon black, swirl, and then remove the latter by filtration through a large fluted filter paper. Allow the filtrate to cool in an ice bath and filter on Whatman No. 42 paper on a Büchner funnel. If the product is not white, repeat the recrystallization. Finally dry the white crystals overnight in a vacuum desiccator. Keep the product in a refrigerator. Dissolve 0.10 gram of the dried product in 100 ml. of chloroform. Keep the solution in a refrigerator when not in use. Prepare the chloroform solution fresh every 3 or 4 days.

Potassium Iodide Solution. Dissolve 20 grams of potassium iodide in 100 ml. of distilled water.

Sodium Metabisulfite Solution. Dissolve 5 grams of sodium metabisulfite, $Na_2S_2O_5$, in 100 ml. of distilled water. Prepare fresh each day.

Hydrochloric-Nitric Acid Solution. Mix 60 ml. of hydrochloric acid with 40 ml. of distilled water and then add 1 ml. of nitric acid.

Sodium Hydroxide Solution. Dissolve 20 grams of sodium hydroxide in 100 ml. of distilled water.

PROCEDURE

Preparation of Calibration Curve. Transfer 0, 1.0, 2.0, 3.0, 4.0, and 5.0 ml. of standard arsenic solution (1 γ of arsenic per ml.) to 10-ml. volumetric flasks; add 0.2 ml. of perchloric acid, and dilute to 5 ml. with distilled water. Add 1 drop of methyl red solution and neutralize carefully with concentrated ammonium hydroxide, added dropwise from a bottle equipped with a ground-glass medicine dropper stopper, until the solution just turns yellow. Blow out the ammonia fumes from the interior of the flask.

In the succeeding steps the volumes of the various reagents added must be closely controlled, otherwise incomplete color development or reduction of the ammonium molybdate may occur. Add hydrochloric acid (4 to 6) dropwise to bring back the red color and then add 0.5 ml. of this dilute acid in excess. Add 0.2 ml. of the potassium bromate solution and warm and swirl to decolorize the solution. Cool, add 0.5 ml. of ammonium molybdate solution, and swirl to mix. Add 0.5 ml. of hydrazine sulfate solution, dilute to the mark, and mix. Place unstoppered in vigorously boiling distilled water in a 150-ml. beaker on a hot plate and allow to remain for exactly 5 minutes. The water level should be high enough so that the mark on the flask is immersed.

Remove to the bench for a minute or so and then cool to room temperature in two successive water baths. Pour all of the sample through a small funnel into a clean 5-cm. Corex absorption cell. Without delay, measure the sample photometrically at 840 mμ using distilled water as the reference solution; use the red-sensitive phototube and a slit width of 0.015 mm. The 10 ml. of sample solution does not fill the adsorption cell. It is sufficient, however, for the entire height of the light beam to pass through the solution, if the cell carriage is properly leveled. Prepare a calibration curve. The reagent blank should give a transmittancy reading of about 95%. If the reading is much lower than this, prepare fresh reagents.

Analysis of Germanium or Germanium Dioxide Sample. If germanium metal is to be analyzed, first crush it in a clean, rust-free Plattner mortar into pieces not much bigger than the size of a pea. Transfer a small portion of the crushed metal to the Plattner mortar and pound vigorously to break the metal into as fine particles as possible. Remove to the 150-mesh platinum sieve and shake to recover that portion of the sample which will pass through the screen. Return the residue to the mortar and repeat the crushing. Alternately crush and sieve the metal until all of it has been passed through the sieve. Mix well and pass through the sieve a second time to remove any large particles which may have accidentally fallen in.

Transfer 2.000 grams of the sieved germanium to a 250-ml. Vycor conical flask. Add 12 grams of oxalic acid, 25 ml. of distilled water, and 5 ml. of hydrogen peroxide (30%). Carry a reagent blank through the entire analysis. Cover and warm gently, with swirling, to start solution of the sample. When vigorous solution starts, remove the flask from the hot plate and swirl continuously until the vigorous solution ceases and the covered flask can be safely placed on an asbestos pad on a low-temperature hot plate. Continue to boil gently, swirling continually, for about 5 minutes. Add 5 ml. more of hydrogen peroxide (30%) and continue to swirl and heat gently on the plate for a further 5 minutes. Excessive heating should be avoided; otherwise too much of the oxalic acid will be destroyed and germanium dioxide may precipitate. The constant swirling greatly accelerates the solution of the sample and thus reduces the danger of precipitation of oxide.

Finally, when dissolution of the sample has again slowed down, decant the solution to a 250-ml. Vycor conical flask. Do not wash. Add 2 grams of oxalic acid plus 10 ml. of distilled water plus 2 ml. of hydrogen peroxide (30%) to the undissolved residue in the first flask. Cover and heat to gentle boiling, with intermittent swirling, until solution of the sample is complete. Dissolution of 2 grams of germanium metal can be completed in about 20 minutes if the metal has been properly pulverized and the correct solution technique has been followed. Combine the two solutions, add 20 ml. of hydrochloric acid, and dilute to 100 ml. Cover and heat to gentle boiling to destroy the hydrogen peroxide. When gas bubbles cease to be evolved, add 2 grams of oxalic acid, boil gently for 5 minutes longer, and then remove from the plate. Traces of undecomposed hydrogen peroxide will do no harm in the arsenic determination, but appreciable amounts must not be present. If the solution is more than faintly opalescent, filter through a Whatman 9-cm. No. 42 paper. Proceed to the reduction of the arsenic as described subsequently.

If germanium dioxide is to be analyzed, transfer 3.000 grams of the powdered sample to a 250-ml. Vycor conical flask and add 10 ml. of distilled water and 15 grams of oxalic acid. Carry a reagent blank through the entire analysis. Cover and, while swirling occasionally, heat to gentle boiling to dissolve the sample. This usually requires less than 15 minutes. Ignore traces of insoluble material. Do not heat excessively for fear of decomposing too much of the oxalic acid. When dissolution is as complete as possible, add 1 ml. of hydrogen peroxide (30%) and heat for 1 or 2 minutes to complete the solution of the sample. Add 20 ml. of distilled water and 20 ml. of hydrochloric acid, cover, and boil gently for 2 or 3 minutes to destroy most of the remaining hydrogen peroxide. Filter if necessary.

Dilute the solution to 100 ml. and adjust its temperature to 50° C. Add 2 ml. of potassium iodide solution and 2 ml. of sodium metabisulfite solution. Swirl and then transfer without delay to a 150-ml. Squibb-type separatory funnel. Allow to remain undisturbed for 15 minutes to reduce the arsenic. Cool by resting the funnel in a bath of distilled water until the temperature of the solution in the funnel is 35° C. Extract at about 35° C. so as to prevent precipitation of oxalic acid crystals. In the analysis of the germanium dioxide reagent blank it is usually not possible to prevent this precipitation. For this reason it is necessary, in the analysis of this sample, to cool to room temperature after dilution to 100 ml. and filter through a small plug of glass wool on a glass funnel to remove the precipitated oxalic acid. Do not wash, but instead press out the liquid held by the precipitate and funnel stem. Heat to 50° C., reduce, and continue as directed above.

Add 15 ml. of diethylammonium diethyldithiocarbamate solution. Stopper, shake momentarily, release the pressure by loosening the stopper, and then shake vigorously by hand for 1 minute. Wash off the outer and inner walls of the stem of the separatory funnel twice with a fine stream of water from a wash bottle, shaking after each washing, to remove the water in the bore of the stem. Finally, remove the stopper, swirl to detach the drop of diethylammonium diethyldithiocarbamate solution floating on the top of the solution, and allow the two layers to separate for a minute or so. Fill the stem with a fairly compact plug of fine spun borosilicate glass wool and cut off any excess hanging below the stem. Avoid contaminating the glass wool with germanium salts. Drain the diethylammonium diethyldithiocarbamate solution to a clean 50-ml. borosilicate glass conical flask, stopping the flow just before the aqueous layer enters the bore of the stopcock. Wash down the walls of the separatory funnel with about 2 ml. of chloroform from a wash bottle. Stopper, invert, shake for a few seconds, unstopper, swirl, and allow to settle for 1 or 2 minutes. Drain to the 50-ml. borosilicate glass conical flask containing the diethylammonium diethyldithiocarbamate solution, stopping the flow just before the aqueous layer enters the bore of the stopcock. Discard the aqueous layer. Rinse all glassware in cleaning solution and wash well before re-use.

Add 0.5 ml. of perchloric acid and 1 ml. of nitric acid to the 50-ml. flask and swirl to mix. Partially cover with a small watch glass and boil gently on a 175° C. hot plate. The temperature of the hot plate can be determined with the aid of a thermometer, which is suspended in such a way that its bulb is near the bottom of a 15-ml. portion of Dow-Corning No. 550 silicone oil contained in a 30-ml. beaker placed on the hot plate. After the chloroform has been expelled and fumes of nitric acid are being evolved, remove the cover and allow the solution to evaporate until fumes of perchloric acid begin to be evolved. Finally heat

over a Meker-type flame just to copious white fumes to expel most of the nitric acid. Cool, add 2 ml. of hydrochloric-nitric acid solution, and allow to evaporate without cover on the low temperature hot plate until fumes of perchloric acid appear. Heat gently at first and then more strongly over a Meker-type flame until the volume of solution has been reduced to 0.2 ml. Cool somewhat and then wash down the walls of the flask with 2 or 3 ml. of distilled water.

Transfer the solution through a small funnel to a 10-ml. volumetric flask, washing once or twice with a fine stream of distilled water. If the solution contains any dehydrated silica or any other precipitate, make the transfer through a small Whatman No. 42 paper. Excessive washing should be avoided; otherwise there will not be sufficient room left to add the necessary reagents. Add 1 drop of methyl red solution, neutralize, and continue as in the preparation of the calibration curve. With the aid of the calibration curve, determine the weight of arsenic present in the sample and in the reagent blank.

Analysis of Silicon Sample. Powder and sieve the silicon metal as directed above. Transfer 0.5 gram of the 150-mesh silicon metal to a 100-ml. platinum dish. Add 5 ml. of sodium hydroxide solution. Carry a reagent blank through the whole procedure. Cover with a borosilicate glass watch glass and warm the solution on a hot plate. When the violent reaction has ceased, wash down the cover glass with distilled water. Boil gently until all or nearly all of the sample has dissolved, adding a few milliliters of distilled water if the solution evaporates to less than 2 ml. Dissolution of the sample requires about 20 minutes.

Dilute the sample in the platinum dish to 20 ml. with distilled water and add 1 ml. of hydrogen peroxide (30%). Cover and boil until all the peroxide has decomposed. Cool to room temperature and dilute to 50 ml. with distilled water. Make just acid to congo red paper with hydrochloric acid. Filter through a 9-cm. No. 41 Whatman paper into a 150-ml. beaker in order to remove traces of insoluble materials. Wash the dish and paper once with a small portion of distilled water and discard the paper. Add 25 ml. of hydrochloric acid, heat to 50° C., add 2 ml. of potassium iodide solution plus 2 ml. of sodium metabisulfite solution, and proceed to the reduction, extraction, and determination as directed above.

DETERMINATION OF PHOSPHORUS

In order to determine phosphorus, antimony, and copper, the germanium must first be quantitatively removed by distillation as chloride from hydrochloric-nitric acid solution containing a little perchloric acid. In the analysis of germanium metal, it is necessary to dissolve the sample in a hydrochloric-nitric acid mixture containing enough nitric acid to ensure fairly rapid solution without, however, precipitating any oxide. If concentrated hydrochloric acid is used in the solution-distillation of germanium dioxide, the finely powdered oxide tends to be carried up and out of the flask by the gas bubbles that form. By using more dilute acid, this difficulty is overcome. The hydrochloric acid concentration cannot, however, be reduced below about 24% by weight without seriously retarding the solution-distillation of the germanium dioxide. In order to keep the reagent blank to the minimum in the determination of phosphorus, antimony, or copper, it is necessary to redistill the acids used in the analyses.

Precautions must be taken to obtain and keep the phosphorus oxidized to the normal phosphate state and to limit the temperature by taking to fumes of perchloric acid rather than sulfuric acid in the expulsion of germanium. In this manner no phosphorus will be lost by volatilization.

The only sensitive photometric method available for the determination of traces of phosphorus is the molybdenum blue method. The method used for arsenic is equally applicable to phosphorus.

Metals such as selenium, tellurium, tungsten, zirconium, titanium, and vanadium interfere in the classical gravimetric phosphomolybdate method for phosphorus. The authors' experiments, using 50-γ portions of various metals, show surprisingly that tellurium, titanium, and vanadium cause no interference in the photometric phosphorus method. On the other hand, zirconium, tungsten, niobium, tantalum, arsenic, silicon, selenium, and gold interfere in the manner described in the arsenic determination. In addition, copper, even when present in quantities of less than 10 γ, causes very low results. The reason for this is not apparent.

The interference of zirconium, tungsten, niobium, and tantalum can be eliminated by complexing these metals with fluoride, but unfortunately the presence of fluoride ion greatly enhances the interference of silicon. Fluoborate ion, on the other hand, appears, if anything, to suppress the interference of silicon and germanium. When fluoborate ion is added, none of the 56 metals listed above interferes, with the exception of arsenic, selenium, silicon, copper, and gold.

Arsenic and selenium can be removed by distillation as bromide. Silicon can be rendered harmless by dehydration with hot perchloric acid. Copper, even in microgram quantities, can be quantitatively removed by cementation on lead in dilute perchloric acid solution. Iron does not interfere with the deposition, if chloride is absent. Gold will be removed with the copper.

REAGENTS

Sodium Fluoborate Solution. Transfer 5 grams of sodium fluoride plus 30 grams of boric acid to 300 ml. of distilled water in a 500-ml. glass-stoppered borosilicate glass conical flask and shake to dissolve the material. Filter through Whatman No. 40 paper and dilute to 500 ml. with distilled water. Store in a polyethylene bottle.

Standard Phosphorus Solution (1 γ of Phosphorus per Ml.) Dissolve 0.4260 gram of pure dry diammonium hydrogen phosphate in distilled water and dilute to 1 liter in a volumetric flask. Transfer 10.0 ml. of this solution to a 1-liter volumetric flask, dilute to the mark, and mix.

Redistilled Hydrochloric Acid. Transfer 2 grams of ferrous ammonium sulfate, $Fe(NH_4)_2(SO_4)_2.6H_2O$, plus a few silicon carbide granules plus 1000 ml. of hydrochloric acid plus 500 ml. of distilled water, to a 2-liter borosilicate glass round-bottomed flask equipped with standard-taper joint. Connect the flask with an all borosilicate glass distilling-condensing system in a well ventilated hood and distill the acid mixture to remove arsenic. Discard the first 50 ml. of the distillate. Collect and store the redistilled acid in a clean glass-stoppered borosilicate glass bottle. Discard the residual 50 ml. of acid in the distilling flask. When the distillate is well mixed it contains about 24% by weight of hydrochloric acid.

Redistilled Nitric Acid. Distill 1 liter of nitric acid (specific gravity 1.42) in an all-borosilicate glass system, discarding the first and last 50-ml. portions of the acid. Store in a clean glass-stoppered borosilicate glass bottle.

Redistilled Hydrobromic Acid. Distill 1 liter of hydrobromic acid (48%) in an all-borosilicate glass system, discarding the first and last 50-ml. portions of the acid. Store in a clean glass-stoppered borosilicate glass bottle.

Nitric-Hydrochloric Acid Solution (1 to 99). Mix 1 volume of redistilled nitric acid with 99 volumes of redistilled hydrochloric acid. Prepare the mixture just before use.

Nitric-Hydrochloric Acid Solution (1 to 5). Mix 1 volume of redistilled nitric acid with 5 volumes of redistilled hydrochloric acid. Prepare the mixture just before use.

PROCEDURE

Preparation of Calibration Curve. Transfer 0, 1.0, 2.0, 3.0, 4.0, and 5.0 ml. of standard phosphorus solution (1 γ of phosphorus per ml.) to 25-ml. volumetric flasks and dilute to approximately 10 ml. with distilled water. Add 0.5 ml. of perchloric acid followed by 1.25 ml. of sodium fluoborate solution and then 1 drop of methyl red solution. Continue as directed in the arsenic method, using 1.25 ml. of hydrochloric acid, ammonium molybdate, and hydrazine sulfate solutions in place of the 0.5-ml. portions recommended. Use only 0.2 ml. of the potassium bromate solution. Heat in 300 ml. of boiling water in a 400-ml. beaker. The per cent transmittancy of the blank should be in the neighborhood of 85.

Analysis of Sample. Transfer 2.000 grams of 150-mesh germanium to a 125-ml. Vycor conical flask. Carry a reagent blank through the entire analysis. Add 2 ml. of perchloric acid and 50 ml. of nitric-hydrochloric acid solution (1 to 5), cover, and heat to boiling on a medium temperature hot plate (approximately 250° C.). When the violent solution has ceased and most of the remaining granules of germanium have collected on the bottom of the flask, swirl to remove traces of the metal that may be on the

walls of the flask and remove the cover. Boil vigorously until the volume has been reduced to 5 or 10 ml.

Finally when the solution starts to get cloudy, add 15 ml. of redistilled hydrochloric acid, cover, and heat to boiling to redissolve the precipitated germanium dioxide from the walls of the flask. It is essential that the hydrochloric acid be added before the appearance of perchloric acid fumes; otherwise the precipitated germanium dioxide will be very difficult to redissolve. When the volume of the solution has been reduced to approximately 2 ml., remove the cover and continue to heat until copious fumes of perchloric acid just begin to come off, in order to remove most of the remaining nitric acid. Cool slightly, add 15 ml. of redistilled hydrochloric acid, and heat on the hot plate without cover to expel the remaining traces of germanium. Finally, when perchloric acid fumes again appear, cool, add 3 ml. of redistilled hydrobromic acid, and proceed with the expulsion of arsenic, antimony, and selenium as directed subsequently.

To analyze germanium dioxide, transfer 3.000 grams of the powdered sample to a 125-ml. Vycor conical flask. Carry a reagent blank through the entire analysis. Add 2 ml. of perchloric acid plus 50 ml. of nitric-hydrochloric acid solution (1 to 99). Cover and heat to boiling on a low temperature hot plate (approximately 200° C.). Swirl occasionally, if necessary, to break any bubbles that may carry germanium dioxide up out of the flask. Finally, when the germanium dioxide has become wetted and the solution is boiling smoothly, remove the cover and allow the solution to evaporate. Swirl occasionally to loosen the germanium dioxide that tends to collect on the bottom of the flask. When the solution is clear, or nearly so, increase the hot plate temperature somewhat, cover, and continue to boil until all traces of precipitated germanium dioxide on the flask walls have been redissolved. Finally remove the cover and continue to heat until fumes of perchloric acid appear. Heat on a flame until copious perchloric acid fumes just begin to be evolved in order to remove most of the remaining nitric acid. If the distillation has been properly done, no germanium should remain. However, in case of doubt, a further distillation with 5 ml. of redistilled hydrochloric acid may be made. Cool and add 3 ml. of redistilled hydrobromic acid.

Boil down on a flame to a volume of 0.5 ml. to expel arsenic, antimony, and selenium, if present. Cool, add 15 ml. of distilled water, add 0.2 gram of fine grain test lead, cover, and boil very gently for 15 minutes to cement out any copper that may be present. Finally, without removing the sample from the plate, add 1.25 ml. of sodium fluoborate solution, cover, and boil 1 minute to dissolve any precipitated zirconium phosphate. Cool and filter through a 5-cm. Whatman No. 42 paper into a 25-ml. volumetric flask, washing twice with distilled water. Add 1 drop of methyl red solution and continue with the neutralization and color development as in the preparation of the calibration curve. With the aid of the calibration curve determine the weight of phosphorus present in the sample and in the reagent blank.

DETERMINATION OF ANTIMONY

Providing the temperature of the hot plate used does not exceed about 200° C. during the solution-distillation of germanium or germanium dioxide, no loss of antimony occurs. Following the removal of germanium, the antimony is best determined by the highly sensitive photometric rhodamine B–benzene method (*2*). The antimony must be oxidized to the pentavalent state before the addition of rhodamine B, either by oxidizing trivalent or quadrivalent antimony with perchloric acid or by oxidizing trivalent antimony with ceric sulfate. The authors' experience indicates that oxidation with perchloric acid as described by Maren (*2*) is not quite complete and that subsequent treatment with ceric sulfate is required. With this modification, the Maren method and the ceric sulfate method give almost identical results in antimony analyses, but the former method has been recommended in the present work because of its convenience. In addition, the ceric sulfate method suffers from the fact that iridium, if present, precipitates during the reduction with sulfur and causes the results for antimony to be very low. (Gold, thallium, and iron cause high results.) In spite of this, however, the ceric sulfate method is useful in many instances.

Obtain the antimony in 4 ml. of concentrated sulfuric acid in a 125-ml. Vycor conical flask, add about 30 mg. of pure powdered sulfur, take to copious white fumes on a Meker-type flame and reduce the volume to 2.5 ml., cool, add 3 ml. of distilled water, and then boil off almost all of the added water in order to expel sulfurous acid that would otherwise reduce ceric sulfate. Cool, add the hydrochloric and phosphoric acids, and proceed as directed below, retaining the globule of sulfur in the conical flask.

In preliminary tests of Maren's method it was found that if water or dilute phosphoric acid was added before the hydrochloric acid, extremely low results for antimony were obtained, presumably because of hydrolysis of the antimony. With the ceric sulfate method, on the other hand, full color development is obtained regardless of the order of addition of the acids.

No attempt is made in either method to reduce the excess ceric sulfate. It is possible that the rhodamine B itself acts as a reducing agent.

Clarence Zischkau and his associates at the American Smelting and Refining Co., South Plainfield, N. J., have shown that the addition of a little butyl Cellosolve greatly facilitates the extraction of the antimony–rhodamine B compound by the benzene. This modification has been adopted in the method described.

Specificity tests on 50-γ portions of the 56 metals listed above show that in the modified Maren method only three metals interfere. Gold, thallium, and iron react with rhodamine B to produce red colored solutions whose color intensities are about the same, $^1/_2$, and $^1/_{200}$, respectively, of that of antimony. In many cases the interference of iron can be ignored. Fortunately, the interference of the three metals can be easily eliminated. To do this the authors have taken advantage of the fact that trivalent antimony can be quantitatively extracted by a cupferron-chloroform extraction, whereas quinquevalent antimony and monovalent thallium are not extracted at all.

After removal of the germanium, antimony is reduced to the trivalent state and separated from thallium (and most of the iridium) by a cupferron-chloroform extraction; the antimony is then oxidized and iron is removed by a second cupferron-chloroform extraction, gold is removed by precipitation as the metal using selenium as a coprecipitant; antimony is then oxidized with perchloric acid and ceric sulfate and determined by the photometric rhodamine B method.

Some gold accompanies the antimony through the first cupferron separation, presumably in the colloidal metallic state, and thus necessitates the subsequent separation as metal, using selenium as a coprecipitant. Attempts to isolate antimony by coprecipitation with manganese dioxide from dilute perchloric acid solution failed because gold and thallium accompany the antimony.

In the method described below, the samples used for the preparation of the calibration curve are carried through all the separations, in order to compensate for slight losses of antimony that occur in these separations. Fortunately, the losses are small and their sum amounts to only about 10% of the total antimony present.

It would appear that a very sensitive photometric method for the determination of gold can be developed based on the rhodamine B reaction. Thallium produces a fluorescent pink color with rhodamine B, that may also serve as a basis for a photometric or fluorescent method for this metal.

REAGENTS

Standard Antimony Solution (1 γ of Antimony per Ml.) Dissolve 0.1000 gram of pure powdered antimony metal by heating with 10 ml. of sulfuric acid in a 500-ml. borosilicate glass conical flask. When solution is complete, take to copious white fumes to expel sulfur dioxide. Cool and add 300 ml. of cool sulfuric acid (1 to 2). Cool, transfer to a 1-liter volumetric flask, dilute to the mark, and mix. Transfer 10 ml. of this solution to a 1-liter volumetric flask. Add 300 ml. of cool sulfuric acid (1 to 2), dilute to the mark, and mix.

Cupferron Solution. Dissolve 1 gram of cupferron in 100 ml. of distilled water. Prepare fresh daily.

Selenium Nitrate Solution. Dissolve 0.5 gram of pure powdered selenium in 5 ml. of nitric acid by warming gently. Add 10 ml. of sulfuric acid and evaporate to copious white fumes to expel the nitric acid. Cool, add 10 ml. of distilled water, and again evaporate to fumes. Cool, add 100 ml. of distilled water, and mix.

Ceric Sulfate Solution. Dissolve 0.2 gram of ceric sulfate, $Ce(HSO_4)_4$, in 10 ml. of sulfuric acid (1 to 4) by warming gently. Cool, transfer to a 100-ml. volumetric flask, dilute to the mark, and mix. Keep stoppered when not in use.

Butyl Cellosolve Solution. Mix 100 ml. of butyl Cellosolve with 200 ml. of distilled water.

Rhodamine B Solution. Dissolve 0.1 gram of Eastman's rhodamine B in 100 ml. of distilled water. Filter from traces of undissolved material.

PROCEDURE

Preparation of Calibration Curve. Transfer 0, 1.0, 2.0, and 3.0 ml. of standard antimony solution (1 γ of antimony per ml.) to 125-ml. Vycor conical flasks, add 2 ml. of sulfuric acid, and evaporate off the water. Add about 30 mg. of pure powdered sulfur and then boil down on a Meker-type flame to a volume of about 1 ml., using a second flask containing 1 ml. of acid as a comparison. Cool, add 10 ml. of distilled water, and heat to dissolve any insoluble salts. Cool and transfer to a 60-ml. Squibb-type separatory funnel whose stem has been cut off so that only about 1 cm. is left below the stopcock. Dilute the sample to 20 ml., add 2 ml. of cupferron solution, and mix. Add 10 ml. of redistilled chloroform, stopper, and shake vigorously for 30 seconds. Allow the two layers to separate and swirl once to dislodge the floating drop of chloroform. Drain off the lower layer through a plug of fine spun borosilicate glass wool into a 125-ml. Vycor conical flask. Add 4 or 5 ml. more of chloroform, shake a few seconds, and again drain to the conical flask. Discard the aqueous layer.

Add 1 ml. of nitric acid to the sample and boil on a low temperature hot plate until the chloroform has been expelled. Add 2 ml. of sulfuric acid plus 0.25 ml. of perchloric acid and boil down to 1 ml. on a flame to expel all organic matter. Cool and add 10 ml. of distilled water. Heat to dissolve any insoluble salts, cool, transfer to a 60-ml. Squibb-type separatory funnel, and dilute to 20 ml. Repeat the cupferron-chloroform extraction but discard the chloroform layers from the extraction and wash. Transfer the aqueous solution to a 125-ml. Vycor conical flask.

Add 1 ml. of nitric acid and boil down to sulfuric acid fumes. Add 1 ml. of sulfuric acid plus 0.25 ml. of perchloric acid and then boil down to 1 ml. Cool to room temperature, add 1 ml. of selenium nitrate solution, and mix. Add 5 ml. of sulfurous acid solution (6%) and heat to 95° to 100° C. Allow to stand 5 minutes and then filter through a 9-cm. No. 42 Whatman paper to a 125-ml. Vycor conical flask. Wash well with distilled water and discard the paper and precipitate. Boil down to sulfuric acid fumes and then add 3.0 ml. of sulfuric acid plus 0.25 ml. of perchloric acid. Boil down on a Meker-type flame to a volume of 2.5 ml. From this point until the finish of the photometric measurement there should be no delay in the manipulation.

Cool quickly to room temperature. Wash down the inside of the flask with 5 ml. of hydrochloric acid (1 to 1) from a graduated pipet, swirl, and then pour the contents into a 100-ml. volumetric flask. Repeat the process with 8 ml. of phosphoric acid (1 to 99), and pour into the same volumetric flask. Cool the mixed acid solution to room temperature by swirling under a stream of cold water. Add 1 ml. of ceric sulfate solution, stopper the flask, and invert. Add 5 ml. of rhodamine B solution from a graduate, stopper, and invert. Add 1 ml. of butyl Cellosolve solution followed by 15.0 ml. of benzene from a buret. Stopper and shake vigorously for 30 seconds. Pour the solution into a 150-ml. Squibb-type separatory funnel and allow the two layers to separate. Drain off and discard all of the lower layer plus about 0.5 ml. of the benzene layer. Pour the benzene layer through a dry 9-cm. No. 41 Whatman paper into a 5-cm. Corex absorption cell. Without delay, measure photometrically at 565 mμ using benzene as the reference solution; use the ultraviolet-sensitive phototube and a slit width of 0.02 mm. Prepare a calibration curve.

Analysis of Sample. Dissolve-distill the germanium or germanium dioxide as directed in the phosphorus method, using the low temperature hot plate (200° C.) throughout the solution-distillation procedure of either type of sample. When the germanium has been expelled, add 2 ml. of sulfuric acid and take to copious fumes of sulfur trioxide to expel perchloric acid. Cool somewhat, add about 30 mg. of sulfur, and continue as in the preparation of the calibration curve. With the aid of the calibration curve determine the weight of antimony present in the sample and reagent blank.

DETERMINATION OF COPPER

Because of its specificity, the photometric neo-cuproine method of Smith and McCurdy (*4*) is the most attractive method available for the determination of copper. Gahler (*1*) has greatly improved the method by arranging to extract the colored copper compound with chloroform rather than the lighter solvents recommended. Gahler's modification has been used in the present work.

Tests on the specificity of the method were made using the 56 metals listed above. In preliminary work the samples were neutralized to Congo paper (pH 4) before addition of hydroxylamine hydrochloride and sodium citrate. Satisfactory results for copper were obtained in the presence of 50 γ of all the metals except beryllium. When the latter is present very low results for copper are obtained, owing presumably to adsorption of the copper or the copper compound on colloidal beryllium hydroxide. By adding the hydroxylamine hydrochloride and sodium citrate before the neutralization, the difficulty due to beryllium is eliminated and the method is made completely specific for copper.

REAGENTS

Standard Copper Solution (2 γ of Copper per Ml.). Dissolve 0.1000 gram of pure copper in 3 ml. of redistilled nitric acid in a 125-ml. Vycor conical flask. Add 10 ml. of perchloric acid and take to copious fumes to expel all nitric acid. Cool and then dilute to 1 liter in a volumetric flask. Dilute 10.0 ml. of this solution to 500 ml. in a volumetric flask.

Hydroxylamine Hydrochloride Solution. Dissolve 10 grams of hydroxylamine hydrochloride, $NH_2OH.HCl$, in 100 ml. of distilled water.

Sodium Citrate Solution. Dissolve 30 grams of sodium citrate, $Na_3C_6H_5O_7.2H_2O$, in 100 ml. of distilled water.

Neo-Cuproine Solution. Dissolve 0.100 gram of neo-cuproine in 100 ml. of absolute ethyl alcohol. Keep stoppered in a refrigerator when not in use. The reagent has the formula $(CH_3)_2C_{12}H_6N_2.{}^1/_2H_2O$ and is obtainable from the G. Frederick Smith Chemical Co., Columbus, Ohio.

PROCEDURE

Preparation of Calibration Curve. Transfer 0, 2.0, 4.0, 6.0, 8.0, and 10.0 ml. of standard copper solution (2 γ of copper per ml.) to 100-ml. beakers, add 0.5 ml. of perchloric acid, and dilute to 50 ml. with distilled water. Add 2 ml. of hydroxylamine hydrochloride solution, followed by 2 ml. of sodium citrate solution. Neutralize by dropwise addition of ammonium hydroxide until just definitely red to Congo paper (pH approximately 4). Remove the paper and add 2 ml. of neo-cuproine solution.

Transfer the solution to a 150-ml. Squibb-type separatory funnel and add 15.0 ml. of redistilled chloroform. Stopper and shake vigorously for 30 seconds. Allow the two layers to separate. Insert a fairly compact plug of fine spun borosilicate glass wool in the stem of the separatory funnel and drain approximately 14 ml. of the chloroform solution to a 5-cm. Corex absorption cell. The solution should be clear. Measure photometrically at 457 mμ using chloroform as the reference solution; use the ultraviolet sensitive phototube and a slit width of 0.025 mm. Prepare a calibration curve.

Analysis of Sample. Dissolve-distill the germanium or germanium dioxide as directed in the phosphorus method. Reduce the volume to 0.5 ml. on a flame, cool, add 50 ml. of distilled water, and then continue as in the preparation of the calibration curve. With the aid of the calibration curve, determine the weight of copper present in the sample and in the reagent blank.

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Analytical Chemistry of Micro Quantities of Beryllium

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Because of the very toxic nature of beryllium, submicrogram quantities of the element are of biological importance. Colorimetric, fluorimetric, and spectrographic methods used to determine small quantities of beryllium are subject to interferences by other elements, often necessitating a separation scheme to isolate the element before measurement. The fluorimetric method based on the interaction of beryllium with purified morin is the most sensitive chemical determination tested and compares favorably in sensitivity with the spectrographic method. The separation of beryllium from bone proved to be most difficult because of the large quantity of calcium phosphate. Using a combination of steps consisting of precipitation, electrolysis with a mercury cathode, absorption on an ion exchange resin, and complexing with acetylacetone, it was possible to isolate completely the smallest measurable quantity of beryllium from all biological samples. The radioisotope beryllium-7 was employed in the determination of the efficiency of each step of the separation scheme.

THE problems in the determination of beryllium may be divided into three categories: methods of estimation, removal of organic material, and removal of interfering substances. In the subsequent discussion, the various procedures available in each category are presented without regard to any special requirements. These will vary with the needs of the analyst. The authors' interest is in the detection of beryllium in biological material and, because beryllium is so very toxic (*16*), special emphasis is given the analysis of minute samples of the cation by very sensitive methods of detection.

In discussing the sensitivities of the various methods, it is important to bear in mind what the figures mean in terms of total beryllium taken for analysis. Thus, a sample for colorimetric or fluorimetric analysis is usually made up to a minimum volume of 10 ml. by the time the reagent, buffer, and stabilizer are added. In the spectrographic method, the crater on the arc may hold anywhere from 0.1 to 0.5 ml., but this quantity is taken from a sample which has been concentrated to a specified volume (usually 1 ml.).

METHODS OF ESTIMATION

There are three general methods for the determination of microgram quantities of beryllium: colorimetric, fluorimetric, and spectrographic. Many colorimetric methods are reported, for almost any dye which may be used for aluminum may be adapted for use with beryllium. A number of these colorimetric procedures have been investigated in this laboratory, and Table I shows the accuracy obtainable in several of these methods.

The minimum useful range for colorimetric methods is in the 1- to 10-microgram region, although much smaller quantities may be detected. The dyes are nonspecific and the interferences in the alkannin method, shown in Table II, are typical. The reagents alkannin and naphthazarin both have the same chromophoric group and react similarity with beryllium. The conditions for color formation have been studied thoroughly (*22*), and it has been demonstrated positively that complexes are formed by the interaction between the beryllium and the dye (*23*). Depending upon the ratio of dye to beryllium, the complex may exhibit molecular ratios of 1 dye to 1 beryllium or 2 dye to 1 beryllium. Under the conditions employed in the colorimetric determination, the colored compound is the 2 dye to 1 beryllium complex. Alkannin is prepared from an extraction of alkanet root, while naphthazarin is a synthetic product (*21*). Based on the extensive study made on these two dyes, a very reliable colorimetric method has been developed with a sensitivity as great as that of any other colorimetric method yet reported.

The most sensitive chemical test for beryllium is the fluorescence developed by its interaction with morin at pH's greater than 11, and considerable interest (*10, 12, 15, 24*) has been shown in this reagent for estimating small quantities of the element. Commercial morin is of variable and doubtful purity, but a purification scheme has been developed (*5*). With the pure product the sensitivity of the method is increased nearly tenfold (*24*). A serious difficulty universally encountered is the rapid decrease in fluorescence after the reagents are mixed. An alkaline stannite has been used (*10, 12*) to stabilize the fluorescence. As originally described, this stannite solution must be freshly prepared each day. A more permanent stabilizing solution may be prepared by mixing stannite and hydrazine dihydrochloride and storing under nitrogen. A number of reducing agents and bivalent cations have been investigated as stabilizers without success. The mechanism of fading and stabilization remains obscure. Most of the commercial fluorimeters use a mercury vapor lamp giving very intense ultraviolet radiation as the exciting source for the fluorescence. It was felt that this radiation aggravated the problem of fading. After some preliminary studies on the excitation frequencies, it was found that an automobile headlight lamp excited sufficient fluorescence to energize a system consisting of two barrier-layer type photocells and a Leeds and Northrup No. 2430-D (0.00045 μa. per mm.) galvanometer. The light

Table I. Accuracy in the Range 1 to 10 Micrograms

Reagent	Error, γ
Quinizarin-2-sulfonic acid (*7*)	0.1
Aurintricarboxylic acid (*11*)	0.2
Alkannin (*22*)	0.06
Naphthazarin (*22*)	0.06
Eriochrome cyanin R (*20*)	0.05

Table II. Interferences in Alkannin Method (*22*)

(4.65γ Be)

Ion	1 Mg.	0.1 Mg.	0.01 Mg.
Ca	0	0	0
Zn	+	+	+
Al	Ppt.	Ppt.	+
Mg	+	+	0
Cu	Ppt.	Ppt.	+
Fe	Ppt.	+	+
Li	0	0	0
F	−	−	0
PO_4	−	0	0
Cl	0	0	0
SO_4	0	0	0
NO_3	0	0	0

0. No interference.
Ppt. Formation of visible precipitate.
+. Increase in colorimetric reading.
−. Decrease in colorimetric reading.

entered through the bottom and was measured from two sides of a quartz cell 25 mm. square and 50 mm. high containing 10 ml. of solution. Figure 1 shows a working curve obtained under the most sensitive conditions (limitations are imposed by the size of the blank). On the working curve the blank reading has been adjusted to a minimum on the galvanometer. The actual blank reading obtained against distilled water was 45 mm., while a sample containing 0.01 γ of beryllium in the 10-ml. final volume gave a reading of 32 mm. above the blank.

Table III. Comparison of Sensitivities

	Microgram
Colorimetric (*22*)	0.2 ± 30%
Fluorimetric	0.004 ± 20%
Spectrographic	
On arc	0.002 ± 50% (*2*)
	0.0005 (*18*)
Spark (*17*) (2 ml.)	0.004 ± 50%

Table IV. Recovery of Beryllium-7 Added to Various Salts

Salt	Be Carrier Added, γ	Treatment	Recovery, %
HCl, 1 ml.	20	Evaporated to dryness with infrared	102
	20	Ignited at 750° for 17 hours	102
NH_4Cl, 1 gram	20	Ignited at 750° for 17 hours after driving off NH_4Cl carefully	99.2
	20	Evaporated to dryness with infrared	99.7
NA_2HPO_4 1 gram	20	Ignited at 750° for 17 hours	98.4
NaCl, 1 gram	20	Ignited at 750° for 17 hours	103
5 *N* HCl	Carrier-free	Evaporated with infrared lamp and ignited at 500° for 1 hour	100.3

The spectrographic method (*2, 6, 14, 17, 18*) will determine the smallest quantities of beryllium, but transposed into quantities which must be actually present in a sample, the fluorimetric method is comparable. Table III shows a comparison of the sensitivities of the three methods of analysis. The quantities for the colorimetric and fluorimetric methods are actual amounts present in the final 10-ml. volume. In the arc spectrographic method, the quantities shown must actually be in the arc. This quantity is usually taken from a minimum final volume of 1 ml. (*6, 14, 18*), although a method has been developed (*2*) where the entire sample is evaporated to dryness under carefully regulated conditions and scraped into the crater.

All three methods—colorimetric, fluorimetric, and spectrographic—are subject to interferences, and it is necessary to employ some kind of separation scheme. In dust samples (*14*) a separation scheme is necessary for the spectrographic method in order to obtain a more uniform matrix for excitation rather than to eliminate spectral interferences. The separation scheme also serves to extend the usefulness of the quantitative methods by concentrating the element. Since the interferences are many for the colorimetric and fluorimetric methods, the separation schemes essentially isolate the beryllium. The fluorimetric method using morin has the advantage over many of the colorimetric methods, in that aluminum does not interfere and need not be separated.

Biological materials such as urine, blood, soft tissues, and bone may, in some cases, contain micro quantities of beryllium. Determination of beryllium in such samples has been the subject of a number of papers (*6, 9, 10, 12, 14, 17, 24*), each of which contains a slightly different separation scheme. Many of the methods (*6, 14, 17, 24*) are applicable only to the determination in urine or dust samples. Because of the large quantity of calcium phosphate present, bone poses much more of a problem than does other biological material. A study has been made to determine the completeness of each step in a separation scheme (*19*), and this will serve as a basis for the present discussion.

All the separation schemes involve all or part of the following steps which are applicable to the separation of beryllium from bone:

1. Ash to remove organic matter.
2. Dissolve and remove calcium or phosphate.
3. Collect beryllium.
4. Remove cations by mercury cathode or oxine extraction.
5. Separate beryllium from alkali and alkaline earth metals.
6. Collect beryllium for measurement.

ASHING

Organic material may be removed by wet or dry ashing. Dry ashing seems to lend itself to routine work more readily and is usually favored. It has been reported (*6*) that the direct ashing of urine at temperatures as low as 500° C. resulted in losses as high as 87% of the beryllium when a platinum dish was used. Another source (*14*) reported losses up to 90% when the sample was treated first at a low temperature followed by a few minutes in a muffle at 900° C. Such losses were not observed by Underwood and Neuman (*22*) in their standardization of a solution of beryllium metal dissolved in hydrochloric acid. They found that exactly the same results were obtained in evaporating such a solution to dryness and igniting to the oxide whether sulfuric acid had been added or omitted.

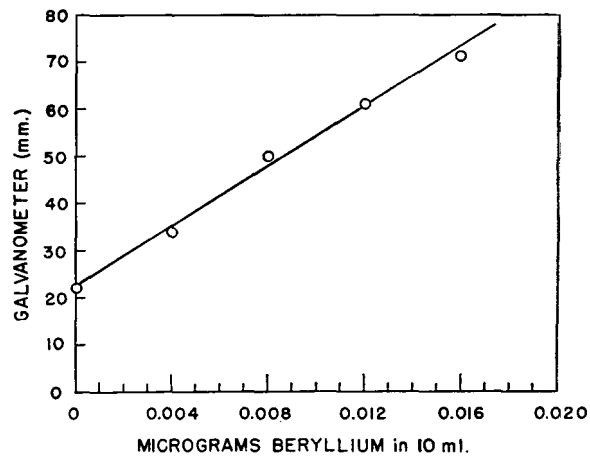


Figure 1. Fluorimetric Response of Beryllium-Morin Solutions

Ashing conditions have been carefully studied (*19*), with the conclusion that no losses by volatilization occur when an aqueous solution of beryllium is evaporated and ignited at temperatures as high as 750° C.

Microgram quantities of beryllium to which the radioisotope beryllium-7 was added were mixed with 1-gram quantities of the main salt constituents of urine. These solutions were evaporated to dryness in platinum dishes under an infrared lamp and then placed in a muffle furnace at 750° C. The samples were removed from the platinum by evaporating with hydrofluoric acid to fumes of sulfuric acid and diluting with water. Measurement of the activity with a dipping tube counter gave the results in Table IV. Longer heating at 750° C. with periodic measurements showed no loss of beryllium activity over an 8-day period. Samples of urine were ignited under conditions for which losses had been previously reported (*6*), with the results shown in Table V.

Samples which had been ignited at 750° C. could be removed from the platinum dish by the hydrofluoric evaporation, but the beryllium could not be absorbed on a cation exchange column nor extracted into benzene with acetylacetone. After the salts had been heated strongly with concentrated sulfuric acid for several minutes it was possible to absorb the beryllium from solution with a cation exchange resin and to extract it with acetylacetone. It is believed that losses previously attributed to volatilization were poor recoveries caused by conversion of the beryllium to a relatively insoluble oxide. Samples of bone which had been

Table V. Recovery of Beryllium from Urine

(50-ml. urine samples dry-ashed in platinum dishes)

Temperature, ° C.	Method of Solution	Be Added, γ	Average Recovery, %
500	Concd. H_2SO_4 heated strongly	4.03	95
500	Concd. HCl	4.03	96
750[a]	HF and H_2SO_4 evap. to fumes of sulfuric	4.03	92
750[a]	HF and H_2SO_4 evap. to fumes of sulfuric	8.06	102

[a] Samples could not be extracted with acetylacetone.

ashed at 600° C. gave no trouble. To preclude the possibility that the beryllium might behave differently after having been ingested in an animal, the radioisotope beryllium-7 with and without carrier was injected into rabbits. Complete recoveries were obtained after ashing the urine, soft tissues, and bones of such animals.

For small samples of urine (50 ml.), tissues, and filter papers containing dust, a wet-ashing procedure using nitric and sulfuric acids (*2, 6, 14*) or nitric and perchloric acids (*14, 17*) is often used. For large quantities of urine, perchloric acid should not be used because of the large quantities of potassium present. For large quantities a semidry technique using nitric acid only has been described (*19*).

In this procedure 500 ml. of urine are evaporated almost to dryness after the addition of 25 ml. of concentrated nitric acid. Toward the end of the evaporation the sample starts to foam and puffs of smoke appear. The reaction is self-sustaining and may be spectacular, varying from a small amount of scintillation to a strong blue continuous flame with much volatile matter evolved. The volatile material does not carry any beryllium with it. Any remaining organic matter is oxidized by further evaporations with 10-ml. portions of concentrated nitric acid. This is a rapid procedure, as a sample may be completely ashed in 1.5 hours.

ISOLATION OF BERYLLIUM

When the beryllium content is extremely low, it is necessary to take a large sample. Following the removal of organic matter, the beryllium is separated from the bulk salts by some gathering procedure. Most commonly some collecting precipitate is formed in the presence of a suitable cation by raising the pH. In the case of a bone solution, raising the pH precipitates a large quantity of calcium phosphate, which carries down most of the beryllium. The bulk of either the calcium ion or the phosphate ion must be removed prior to the gathering step. Precipitates formed in strong acid solution do not carry any beryllium with them. Calcium is best removed as the sulfate from acid solution (*10, 19*) to which alcohol has been added to decrease the solubility. Calcium has also been immobilized by complexing with ethylenediaminetetraacetate (*2*), although this scheme would not be suitable if a collecting precipitate was to be used, as the collecting cation would be complexed and form no precipitate. Phosphate has been removed from acid solution as the bismuth salt (*12*); the excess bismuth ion must be removed as the sulfide. Phosphate may be removed quantitatively from an acid solution by passing the solution through a column of Dowex 50 resin converted to the bismuth form. However, part of the beryllium is also retained by the column, and the procedure is worthless as a separation.

Among the collecting precipitates used are calcium phosphate (*2, 6, 19*), ferric phosphate (*10, 12*), aluminum phosphate and aluminum hydroxide (*10, 24*), and manganous phosphate (*17*). It is reported that the slightest noticeable precipitate of calcium phosphate (*2*) or manganous phosphate (*17*) collects the beryllium quantitatively. This is true, provided there is sufficient beryllium present. When 0.1 microgram of beryllium was added to 10 grams of bone ash (*19*), a maximum of 70% of the beryllium was gathered by calcium phosphate. With 1.3 micrograms of beryllium added to 10 grams of bone ash, 95% of the beryllium was collected under the same conditions.

The most quantitative collecting procedure of those tried is to use a cation exchange column in the hydrogen form. A bone ash sample is dissolved in dilute hydrochloric acid, and most of the calcium is removed by precipitation as the sulfate. The filtrate is diluted to give an acidity of approximately 0.5 *N* and passed through a Dowex 50 column in the hydrogen form. If sufficient resin is used to absorb all polyvalent cations present, quantities of beryllium as small as 10^{-10} gram (carrier-free radioisotope) are absorbed completely. The cations may then be stripped from the column with 5 *N* hydrochloric acid. The effect of complexing anions depends upon the pH, as shown in Table VI. The lower pH is approximately that of a 1-liter dilution of 10 grams of bone ash, from which the calcium has been removed by precipitation with sulfuric acid. The higher pH is that at which oxine and acetylacetone extractions are usually carried out. At pH 5.0 tetrasodium ethylenediaminetetraacetate is a very poor complexer of beryllium, while phosphate is a very effective one. It is probably the HPO_4 ion which is effective in complexing the beryllium, as there is no interference to absorption of beryllium (in the presence of phosphate) at pH 1.8.

The mercury cathode is very convenient for removing many cations (*10, 12, 13, 19*). Oxine (8-quinolinol) is used to precipitate iron, aluminum (*14, 24*), and other metals from acetate-buffered solutions. A simpler technique is to extract the metal oxinates with chloroform (*13*). This reagent is especially useful for the colorimetric methods in which aluminum interferes.

As a final step in the separation scheme it is necessary to collect the beryllium in the desired volume for analysis. Aluminum, which does not interfere in the fluorimetric method of analysis using morin, is the most used gathering agent (*10, 12, 24*). A more rapid and absolutely quantitative method for collecting the smallest measurable amounts of beryllium (carrier-free isotope) is an extraction of the acetylacetonate into benzene (*19*). Beryllium forms a well-characterized and very stable compound with acetylacetone (*1*). This compound was first applied to the separation of milligram quantities (*8*), then to microgram quantities (*13*), and finally to the preparation of carrier-free beryllium-7 (*3*). In carrier-free quantities evaporation of a benzene solution of the acetylacetonate to dryness resulted in significant losses of activity. Thenoyltrifluoroacetone forms a similar compound with beryllium (*4*), which is nonvolatile and has been used for the preparation of carrier-free beryllium-7. The acetylacetonate is readily decomposed by acid, as evidenced by the complete back-extraction of beryllium into the aqueous phase when the benzene

Table VI. Absorption of Carrier-Free Beryllium-7 by Dowex 50 (NH_4)

pH	Additions per Liter	Be Absorbed, %
1.8	0.057 mole H_3PO_4	105
1.8	0.057 mole Na_2HPO_4 and HCl	100
2.0	4 ml. acetylacetone	79
5.0	0.057 mole H_3PO_4 and acetate buffer	2.8
5.0	4 ml. acetylacetone	15.5
5.0	2.0 grams tetrasodium ethylenediaminetetraacetate	97

Table VII. Extraction of Carrier-Free Beryllium-7 in the Presence of 6.1 Grams of Phosphate at pH 4.5

	Extraction	Minutes Stirred with Acetylacetone	Extracted, %	
1.	1st	5	51	95
	2nd and 3rd	40	44	
2.	1st	30	80	97
	2nd	25	17	
3.	1st	40	82.3	95.4
	2nd	30	13.1	
4.	1st	90	86.5	100
	2nd	45	13.5	

solution is shaken with 5 *N* hydrochloric acid for a few minutes. The thenoyltrifluoroacetonate is very stable, and the back-extraction of beryllium into the aqueous phase is complete only after 80 hours when concentrated hydrochloric acid is used (*4*). The acetylacetonate lends itself more readily to a rapid separation scheme.

Conditions for using acetylacetone vary. For separation in presence of other complexing anions, it is desirable to use as low a pH as possible. If the pH is too low, beryllium acetylacetonate will not be formed. At the higher pH's the greater ionization of the acetylacetone favors its solubility in the aqueous phase and increases the difficulty of extraction of beryllium acetylacetonate into the organic phase. One procedure (*8*) recommends a pH between 3 and 4, another (*13*) recommends 4.5, while a pH of 6 was used in the preparation of carrier-free beryllium-7 (*3*). All these procedures used a benzene solution of acetylacetone to extract the beryllium from the aqueous phase. In the preparation of the radioberyllium, an extraction time of 2 hours was used. A more thorough study of the extraction procedure (*19*) showed that a pH between 4 and 5 was more suitable than the lower range. Further it was shown that stirring the aqueous phase with acetylacetone for 5 minutes before addition of the benzene was more effective than using a benzene solution of acetylacetone. Stirring with a propeller tilted to force the liquid downward gave much more reproducible results than did manual shaking, and a total extraction time of 15 minutes was sufficient.

The extraction time is a function of the anions present in solution. With a small quantity of phosphate (50 to 100 mg. as PO_4) present, complete separation of beryllium is obtained with one 15-minute extraction (5 minutes with acetylacetone plus 10 more minutes after adding benzene). Table VII shows some results obtained when none of the phosphate from 10 grams of bone ash was removed.

The back-extraction of the beryllium into hydrochloric acid takes a small quantity of acetylacetone, which is sufficient to interfere in the final measurement. The acetylacetone may be removed by evaporating the acid solution and igniting gently (below 600° C., or heating with a burner just enough to burn the organic material). The beryllium is then taken up in a small amount of hydrochloric acid. The acetylacetone step removes the alkaline earths and the alkalies. Iron and aluminum also form complex acetylacetonates, which are soluble in benzene. Iron is removable in a mercury cathode. Aluminum need not be removed if the morin method is used. It may be removed with oxine.

DISCUSSION

The choice of a method depends upon the quantity of beryllium and other ions present in the sample. If the quantity of sample is not limited, a separation scheme may isolate sufficient quantities of beryllium to allow any method to be employed. Of the colorimetric methods tried, the alkannin or naphthazarin method (*22*) has been found most reliable. The fluorimetric method using purified morin is more sensitive and aluminum does not interfere. As fluorimetry approaches the spectrographic method in sensitivity, its use should become more general. Purified morin may be obtained easily in several steps, starting with morin obtained from T. Schuchardt, Ltd., Leopoldstrasse 4, München 23, Germany.

The determination of beryllium may be carried out on a large sample of urine with the semidry-ashing procedure (*19*). As the volume has been reduced greatly during ashing, it is unnecessary to use a preliminary gathering step. Electrolysis to remove most of the cations, followed by the use of acetylacetone to complete the separation, makes a relatively simple procedure. Seven 500-ml. samples of urine each containing 1.3 micrograms of beryllium and radioisotope beryllium-7 were carried through this separation scheme with recoverages ranging from 97.5 to 101.7% (average 99.9%). Two samples containing carrier-free radioisotope beryllium-7 gave recoveries of 96.6 and 100.3%.

For bone, dry ashing at 600° C. is most rapid. After calcium removal as the sulfate, the most quantitative gathering procedure is to pass the acid solution through a Dowex 50 column in the acid form. If the bone contains more than 0.1γ of beryllium per gram of ash, the metal may be gathered with a calcium phosphate precipitate obtained by raising the pH of the solution, from which most of the calcium has been removed as the sulfate. After solution in sulfuric acid, the separation of the beryllium is completed by electrolysis using a mercury cathode followed by the acetylacetone extraction. Recoveries between 95 and 98% have been obtained for quantities of beryllium as small as the carrier-free radioisotope (less than 10^{-10} gram).

For soft tissues such as the liver, kidney, and spleen, wet ashing with nitric acid and finishing with perchloric acid are very satisfactory. Using the same separation procedure as for ashed urine, complete recoveries of carrier-free radioisotope have been obtained.

CONCLUSION

Adequate methods are available for the determination of extremely small quantities of beryllium, although all suffer from interferences. Rapid procedures have been developed to isolate the beryllium. A little more work remains to be done to develop the ultimate sensitivity of the fluorimetric method using morin, the limitation being imposed by the size of the blank of the purified reagent. The ideal reagent would be specific for beryllium, one which in itself did not fluoresce but produced an appreciable stable fluorescence in its interaction with beryllium. The ultimate sensitivity for such a reagent would be limited only by the electronic devices available for measuring the light emitted.

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Analytical Chemistry of Uranium

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Advances in the analytical chemistry of uranium from 1949 to the present are reviewed. In addition to papers on gravimetric, volumetric, colorimetric, fluorimetric, and radiochemical methods, x-ray absorption and coulometric procedures have been described for the first time.

THE present interest in uranium as a fissionable material has evolved considerable investigation of the determination of this element. The interest is such that the range runs the entire gamut from amounts as small as 10^{-11} gram per gram to practically 100% pure uranium.

The methods used up to 1949 have been reviewed (*60, 61*). The progress since this time is discussed here. In addition to papers on gravimetric, volumetric, colorimetric, fluorimetric, and radiochemical methods, x-ray absorption and coulometric procedures have been described for the first time.

Methods have been reviewed by Hecht (*37*), and methods for use in mineral products have been published by Burstall and Ryan (*8*), Burstall and Williams (*10*), and Rabbitts (*57*).

SEPARATIONS

Practically all recent advances in methods of separation have been in the use of organic solvents. Some of the work done during the war on the effects of salting agents on the ether extraction of uranyl nitrate (*30*) as well as the extraction of uranous cupferrate with ether (*28*) has been published by the Atomic Energy Commission. Scott (*65*) has studied the effects of salting agents on the extraction of uranyl nitrate with ether. A solution 1 *M* in ferric nitrate and 3 *N* nitric acid has been found most suitable for his work. Kaufman and Galvanek (*42*) have studied the extraction of uranyl nitrate with ether to show how elements which interfere in the alkaline-peroxide colorimetric method can be removed. They devised a simple piece of apparatus in which the sample is roasted, leached, and extracted.

The greatest advance in solvent-extraction work has come from England, where studies on the use of paper strip and packed cellulose columns have resulted in time-saving procedures. Initially paper strips were used (*1, 7, 47*), whereby uranyl nitrate is dissolved and moves with the solvent front as diffusion in the absorbent paper proceeds. Most other metals remain stationary or move only slowly in comparison with the uranium. The uranium in the paper section could then be measured with the polarograph, colorimeter, or fluorimeter. Work on somewhat similar lines with different solvents has been reported by Lacourt, Sommereyns, and Soeté (*46*).

In an excellent series of articles (*9, 44, 54, 63, 71, 75*) an extensive study of variables employing the cellulose column was reported. It was found that activated alumina retained arsenic and molybdenum, which were extracted to some extent when cellulose columns alone were used.

Ferric nitrate may be used to complex phosphate so it will not interfere. The procedure is simple (*63*).

After the walls of the vessel have been coated with a silicone (DOW DC-200), 5 or 6 grams of cellulose pulp (Whatman) are mixed with ether containing 5% nitric acid and poured into the glass tube. After agitation and gentle pressing down to form a column, 15 grams of activated alumina (200 mesh) are added on the top of the cellulose. The sample is dissolved in nitric acid and evaporated to dryness, then taken up in 4 ml. of 25% nitric acid. The solution is absorbed with cellulose, which is then transferred to the top of the column. After extraction with about 200 ml. of ether containing 5% nitric acid, the uranium is entirely in the ether solution and can be determined in any manner desired.

Results obtained are comparable with other accepted methods. The method may also be used in the presence of thorium (*75*). In this case after phosphate has been complexed with ferric nitrate, the uranium is extracted with ether containing 1% nitric acid, and then the thorium nitrate is extracted with ether containing 15% nitric acid. The method has been applied (*45*) to the separation of microgram quantities of uranium. As little as 5×10^{-7} of uranium has been separated.

In another application of solvent extraction, tantalum and niobium (*50*) are separated from uranium in an alloy by extracting the fluorides of the earth acids with methyl ethyl ketone; the aqueous solution contains the uranium.

The effectiveness of different solvents for extracting uranyl nitrate was shown by Spence and Streeton (*72*), who also describe a micro-form rotary extractor.

GRAVIMETRIC METHODS

Gravimetric methods are occasionally used for the determination of uranium. Duval (*22*) has used his thermal balance for studying uranium compounds. Isatin β-oxime (*38*) and 8-quinolinol (*14*) have been re-examined as precipitating agents. If an oxine wash solution instead of water is used, correct results are obtained. Ammonia has been used for the analysis of cobalt-uranium alloys (*49*).

VOLUMETRIC METHODS

The main advances in volumetric methods have been in the choice of methods of reduction. Cooke, Hazel, and McNabb (*17*) have used a lead reductor in hydrochloric acid solution to reduce uranium(VI) to uranium(IV). In this fashion the air-oxidation step is avoided. High concentrations of sulfate can be tolerated, provided a sufficient concentration of hydrochloric acid is present. Sill and Peterson (*68*) also used a lead reductor for milligram amounts of uranium. The size of the lead particles and temperature of the reductor were shown to be important. Furman, Bricker, and Dilts (*29*) used a cadmium amalgam reductor to reduce uranium(VI) to uranium(IV) in a sulfuric acid medium. For solutions containing phosphates Schreyer and Baes (*64*) have used a Jones reductor with 4.5 *M* sulfuric acid to avoid phosphate precipitate. The reduction of uranium(VI) to uranium(IV) was shown to be quantitative in phosphate solutions. Rowe (*62*) showed that arsenate ion does not interfere in the procedure using the Jones reductor.

Chromous salts have been used to reduce uranyl solutions. Hahn and Kelley (*35*) reduced uranyl solutions with chromous

sulfate followed by a potentiometric titration of uranium(IV) with ceric sulfate. The method can be used in the presence of iron by complexing the iron(II) formed with 1,10-phenanthroline. Cooke, Hazel, and McNabb (*18*) used chromous chloride for reduction of milligram quantities of uranium(VI) to uranium(IV) destroying the excess chromous ion by air oxidation. This is followed by the usual ceric sulfate titration.

Sill and Peterson (*68*) have made a study of the usual volumetric procedure (*60*) using the Jones reductor. The effect of small amounts of impurities, time, temperature, and acids on the air oxidation of uranium(IV) as well as the effect of phosphoric acid was investigated. Procedures are given for milligram quantities of uranium. Bricker and Sweetser (*6*) used a cadmium amalgam reductor, followed by a spectrophotometric method for determining the end point when titrating with ceric sulfate.

COLORIMETRIC METHODS

Rasin-Streden (*58*) has given a photometric method using hydrogen peroxide and sodium carbonate which has been used for from 0.2 up to 85% U_3O_8. Scott (*66*) showed that sodium bicarbonate caused errors in the carbonate-peroxide method. Kaufman and Galvanek (*42*) studied the effects of variables employing an ether extraction of uranyl nitrate followed by the alkaline peroxide method. Brackenbury (*5*) has given a plant control procedure using alkaline peroxide.

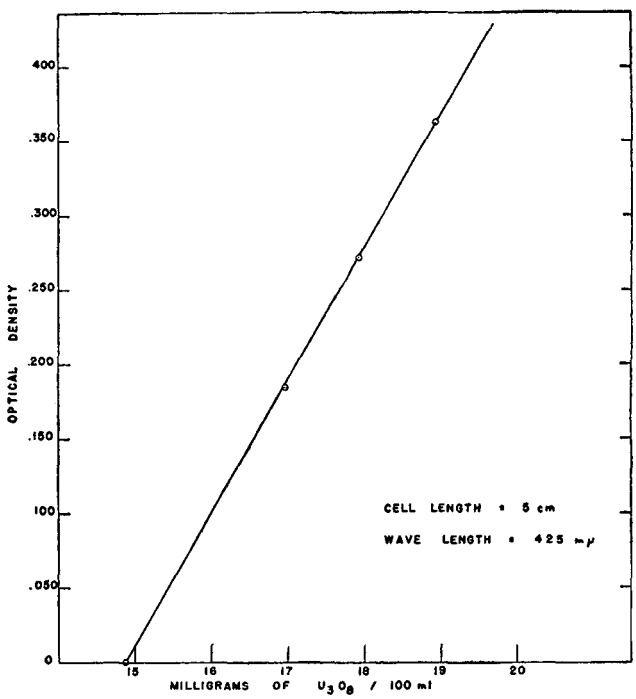


Figure 1. Range of Colorimetric Analysis

By measuring the uranium alkaline peroxide solution against a known amount of uranium treated in the same manner in the blank cell, it is possible to extend the range normally employed and also increase the precision of the analysis. Figure 1 shows such a curve. Using a wave length of 390 mμ and 10-cm. cells it is also possible to extend the peroxide method down to 100 γ. Figure 2 shows the range when 10-cm. cells are used.

Davenport and Thompson (*21*) have used ammonium thioglycolate in a solution of pH 7 to 11 in the range of 0.1 to 1.6 mg. per 25 ml. Beer's law is obeyed. The interfering elements are described. In general, an ether separation prior to the analysis would remove interfering elements.

Gerhold and Hecht (*31*) have used potassium thiocyanate in strong hydrochloric acid. With 30 ml. of 3 *N* potassium thiocyanate and 15 ml. of hydrochloric acid in 100 ml. reproducible results are obtained. The solutions appear to be stable for a sufficient time. Interfering elements are removed by an ether extraction of the nitrate.

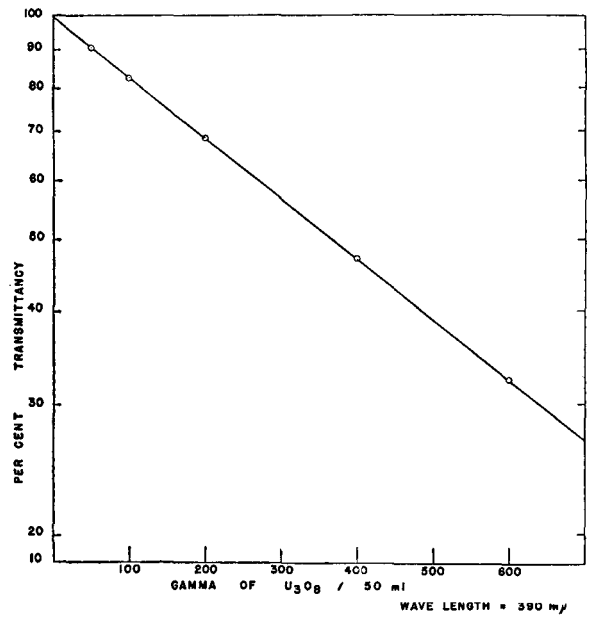


Figure 2. Range of Analysis

Cell length 10 cm.
Wave length 390 mμ

Crouthamel and Johnson (*16*) have employed the thiocyanate reaction in an acetone medium. The stability of the color is improved, the effect of acid concentrations is minimized, and many elements which interfere in aqueous medium do not interfere in the acetone medium. A convenient range is 1 mg. of uranium per 25 ml. at 375 mμ. A differential application is also described. The precision is increased and standard deviation not greater than ±0.25% was obtained. The thiocyanate should be recrystallized from methanol and air-dried before storing (*15*).

Silverman (*69*) has used a chloroform extraction of uranium 8-quinolate and is able to measure 0.05 mg. of uranium even in the presence of iron.

COULOMETRIC METHODS

Two articles have recently appeared (*12, 29*) on the coulometric determination of uranium. One by Carson (*12*) is used on a routine basis at the General Electric Co., Richland, and also at the Argonne National Laboratory. In this procedure the uranium(VI) is reduced to uranium(IV) using a lead reductor. Electrolytically generated bromine in the presence of iron is used to oxidize the uranium(IV) to uranium(VI). Iron bromide (0.02 *M* iron) in 3 *M* hydrobromic acid is used to rinse out the uranium from the reductor. Lead phosphate and sulfate are soluble in this medium. The reduced solution is heated to 95 °C. and the electrolysis started using the derivative polarographic indicator system (*59*). With care, as little as 2 micrograms of uranium can be determined. The method lends itself to the automatic titration procedure of Carson (*11*).

The other method described by Furman, Bricker, and Dilts (*29*) uses a cadmium amalgam reductor to reduce uranium(VI) to uranium(IV). The uranium(IV) is oxidized by ferric sulfate,

and ceric ions are generated electrolytically to oxidize the ferrous ion produced. The analysis is run at room temperature, and with the cadmium amalgam reductor it is not necessary to wash with iron bromide as above. The procedure is applicable to amounts of uranium as low as 5 γ.

POLAROGRAPHIC METHODS

The polarographic method is used to a considerable extent, usually hydroxylamine hydrochloride and sodium tartrate or ammonium citrate being employed. Phosphoric acid interference may be removed by fuming with sulfuric acid (*48*) or by using ferric ion (*4*).

X-RAY METHODS

A determination of uranium using x-ray absorption may be of interest. Bartlett (*2*) showed that elements of low atomic weight did not interfere, and that with cells 19 mm. long the lower limit of detection was 0.1 gram per liter. Chemical separation was necessary where appreciable quantities of other elements were present. Peed and Dunn (*55*) have done preliminary work on using the absorption method for 150 to 30,000 p.p.m. of uranium in water.

Another interesting application of x-rays is Birks and Brooks' (*3*) determination of 0.05 gram per liter of uranium by x-ray fluorescence. Heavy elements such as lead interfere but light elements have no effect. Solids are used by evaporation of liquids into spherical cups. About 10 minutes for each determination is all that is necessary.

SPECTROGRAPHIC METHODS

Kaufman found that the spectrographic determination of uranium in ores was not satisfactory (*43*); the sensitivity was only 0.05% U_3O_8 and it was subject to many interferences. Chemical separation was usually necessary, after which a colorimetric or fluorimetric analysis is more convenient. Strasheim (*73*) has (*a*) used direct evaporation of the sample in a direct current arc, (*b*) extracted uranium and then following as in (*a*), and (*c*) used an enhancing agent in the direct current arc. An accuracy of 11% is claimed by an extraction procedure recommended where calcium is high.

RADIOCHEMICAL METHODS

The determination of uranium in ores by a counting method is used chiefly as a means of obtaining the range Generally this is followed by a colorimetric or fluorimetric analysis. Hardy (*36*) has described a rapid method using a scintillation detector and ratemeter counter. By simultaneous measurement of β and γ activities it is possible to determine uranium and thorium in ores (*23*).

Curie and Faraggi (*19*) have determined uranium and thorium in minerals by irradiating with thermal neutrons. A nuclear emulsion is used to observe the fission tracks; α-particle autoradiography permits determination of thorium by difference. The method has been used on autunite, uranite, and euxenite with a precision of about 6%. For determining uranium in rocks with as little as 0.0003% uranium, Smales (*70*) has used neutron irradiation in the Harwell pile. After irradiation, the barium fission product is separated and counted. The results show good agreement with chemical methods of analysis. The method is suggested where only small amounts are available. The chemical manipulation appears to be more than in the usual fluorescence analysis. The method has been extended (*67*) for use in determining U^{235} in naturally occurring uranium isotopes.

FLUORIMETRIC METHODS

The fluorimetric method is by far the most sensitive for the determination of uranium and is used by a large number of workers. Generally the uranium sample is fused with sodium fluoride or a mixture of sodium fluoride and sodium-potassium carbonate, and the resultant disk is measured in a fluorimeter.

The excellent work of Price, Ferretti, and Schwartz (*56*) which was done during the war has finally been published. This is a thorough investigation of the fluorimetric procedure and describes a fluorimeter which is so sensitive that quenching impurities can be decreased by dilution and which still has sufficient sensitivity for the uranium. The technique described has been used by a large number of workers. Unfortunately, many workers have found that contamination is a very serious problem with the dilution technique, and a solvent purification had to be employed prior to the determination.

The question of fluorimeters is a rather complicated one. It almost appears that every worker designs his own fluorimeter. Numerous fluorimeters are used (*13, 20, 24, 26, 39, 41*), practically all of which employ a source of ultraviolet light with a filter. This light strikes the sample, and the fluorescent light given off after passing through a filter to remove ultraviolet light then impinges on a photocell, generally of the photomultiplier type. Fletcher, May, and Anderson (*27*) have employed a transmission fluorimeter whereby the ultraviolet light passes through the fused disk.

Several studies have been made of the variables encountered in fluorescence analysis (*25, 39, 40, 56, 74*). Jacobs (*39*) has shown that with a 5% sodium fluoride–95% sodium–potassium carbonate fusion mixture variations in fluorescence were noted when the concentrations of calcium, magnesium, tellurium, antimony, vanadium, beryllium, aluminum, and molybdenum increased. His conclusions were that the dilution techniques of Price, Ferretti, and Schwartz (*56*) should be used with caution. The quenching action of iron on uranium fluorescence (*74*) was shown to be serious and would substantiate the above conclusions.

Other variables have been studied by Fletcher (*25*), who showed that when a 9% sodium fluoride–91% sodium–potassium carbonate fusion mixture was used the temperature of the fusion was important. High temperatures tended to dissolve platinum, which gave low results. She recommended a furnace with controlled temperatures at 650°C. Kaufman (*40*) has found that furnace fusions are dependent on the atmosphere in the furnace and the temperature. In general, it appears the Fletcher burner is more satisfactory. Jacobs (*39*) obtained satisfactory results with both a furnace and an open burner.

Because of the higher sensitivity and lower blank that can be obtained with pure sodium fluoride, this flux was preferred by Kaufman (*40*) to the so-called mixed flux. However, pure sodium fluoride does present a problem because of the high temperatures necessary for fusion (1050° C.). Platinum dishes must be used, but at these temperatures there is some tendency for platinum to be attacked by the flux under oxidizing conditions, and the platinum oxide forms a brown film on the surface of the melt and decreases uranium fluorescence. By proper control of the fusion conditions brown melts can be prevented. Such control is possible in well-equipped laboratories but is somewhat difficult in the mining areas where laboratory facilities frequently are rudimentary. Therefore, for field use, the ethyl acetate extraction procedure given below was adapted to be used in conjunction with the mixed flux and gold dishes.

The following procedure has been tested and proved by Kaufman (*40*).

To a 40-ml. screw-cap vial add 1 ml. of a sample containing between 5 and 50 γ of U_3O_8, 15 ml. of nitrate solution (750 grams of magnesium nitrate monohydrate, 50 ml. of concentrated nitric acid, and 100 ml. of saturated calcium nitrate solution per liter), and 10 ml. of ethyl acetate; shake for 1 minute.

Place pellets of sodium fluoride (approximately 375 mg.) in the platinum dishes.

Allow the ethyl acetate and water layers to separate and pipet out 0.1-ml. aliquots of ethyl acetate to absorb on the sodium fluoride pellets.

Evaporate the ethyl acetate under infrared heaters.

Transfer the platinum dishes to a modified Fletcher gas-air burner and heat the dishes for 3 minutes.

Allow melts to cool on burner, transfer to fluorimeter, measure the fluorescence, and compare with standards.

The original sample can be in nitric or dilute sulfuric acid. If phosphate is present, it is complexed by the addition of ferric nitrate. If the sample contains so little uranium that 5 γ cannot be obtained in 1 ml., the sample is concentrated by evaporation. If the sample is too concentrated, it is diluted with 5% nitric acid before the 1-ml. aliquot is taken.

The fluorescence method has been used for uranium in sea water (*51–53*), low-grade ores (*32, 78, 79*), phosphoric acid (*77*), sulfuric acid (*76*), and shales, lignites, and monazites (*34*). A field method has been described (*33*) in which shales, high-silica rocks, and phosphate rocks are fused directly with a standard flux and the fluorescence is measured directly.

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Solvent Extraction Separations of Zirconium and Niobium

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The extraction characteristics of a variety of solvent systems have been examined for the purpose of finding a method for quickly and efficiently isolating zirconium and niobium from all other fission product elements. The mixed butyl phosphoric acids in di-*n*-butyl ether were found effective for this purpose. Conditions have been established for rapidly and efficiently separating both macro and carrier-free concentrations of these two elements from each other and from nearly all other fission product elements. Application of the solvent system to other separations is indicated. Conditions for simply separating the yttrium from the lanthanum group rare earths have been found.

RADIOCHEMICAL procedures for determining zirconium and niobium in a mixture of fission product elements have been based mainly on precipitation reactions (*1–3, 5*). Development of solvent extraction procedures specific for zirconium and niobium appeared worth while, as it seemed that significant improvement in speed and efficiency of determinations might well be attained by this type of separation. Because solvent extractions are frequently as efficacious for isolating elements at very low as well as at high concentrations, utilization of the results of these studies in separating carrier-free concentrations—i.e., no added carrier—of zirconium and niobium also seemed a definite possibility. Consequently, extraction properties of zirconium and niobium in several organic solvents were investigated. Speed and simplicity of operation and application of results to separations of other elements were sought.

APPARATUS AND MATERIALS

Radioisotopes of all but four of the elements studied (palladium, molybdenum, holmium, iodine) were employed as tracers. The radionuclides used are: Zr^{95}, Nb^{95}, Ge^{69}, Ge^{71}, As^{74}, Se^{75}, Sr^{89}, Y^{91}, Ru^{106}, Rh^{102}, Ag^{111}, Cd^{109}, In^{114}, Sn^{113}, Sb^{125}, Te^{127}, Te^{129}, Cs^{137}, La^{140}, Ce^{144}, and Ta^{182}. They were either purchased from the Oak Ridge National Laboratory or isolated from the appropriate element irradiated with deuterons at the 60-inch cyclotron of the Crocker Laboratory, University of California. In each case carrier-free preparations were obtained either as the purchased item or by special chemical separations on the irradiated material. The organic compounds used were of the best grade supplied by the Eastman Kodak Co., and all other chemicals were of reagent grade quality.

The "butyl phosphoric acid" obtained commercially is a mixture of mono- and dihydrogen butyl phosphate. In the commercial mixtures obtained, these two compounds were in the ratio of about 1 to 1.5, as shown by titration with sodium hydroxide. A 70% solution (*v/v*) of the mixed acids in di-*n*-butyl ether was enriched in the di-*n*-butyl ester by water washings (*6*). Four such washings yielded an ether solution containing 4.5 moles of di-*n*-butyl ester to 1 mole of mono-*n*-butyl ester. This solution was then diluted with di-*n*-butyl ether to obtain either 0.6*M* or 0.06*M* solutions of the di-*n*-butyl ester.

Beta- and gamma-ray counting was done on either standard commercially available Geiger-Müller counters or on proportional counters which utilized 90% argon–10% carbon dioxide as the counting gas. pH and titration curves were measured with a Beckman Model G pH meter and glass electrode.

PRELIMINARY EXPERIMENTS

A variety of compounds under various experimental conditions was studied in search of an extractant for zirconium and niobium. The systems investigated are: acetylacetone; tri-*n*-butyl phosphate; trichloroacetic acid with chloroform as the solvent phase; ammonium thiocyanate with ethyl ether; ammonium thiocyanate plus quinoline with ethyl acetate; 2-nitroso-1-naphthol with ethyl acetate; mandelic acid with ethyl ether, benzene, or amyl alcohol; *m*-nitrobenzoic acid with isobutyl acetate amyl alcohol, or tri-*n*-butyl phosphate; and the mixed mono- and di-*n*-butyl phosphoric acids in *n*-butyl ether. In all experiments the concentrations of zirconium and niobium were 1 mg. per ml. unless otherwise stated.

Acetylacetone did not extract either zirconium or niobium from a 0.7*M* hydrochloric acid solution. Equal volumes of the two phases were used and mixing was for 10 minutes.

Neither zirconium nor niobium was extracted in 10 minutes by chloroform from an equal volume of aqueous solution 0.5*M* in trichloroacetic acid, 0.5*M* in sulfuric acid, and 2*M* in ammonium sulfate.

Diethyl ether (presaturated with thiocyanic acid) did not extract zirconium from 5.0 *M* ammonium thiocyanate solutions which were 1 to 4 *M* in hydrochloric acid and 0.05*M* in oxalic acid; extraction was for 15 minutes and the volume ratio of organic to aqueous phase was 6 to 1. Under these conditions about 30% of the niobium was extracted; the extent of extraction of niobium has been shown to decrease as the niobium concentration increases (*4*). It is quantitative at a concentration of about 1 γ per ml. of niobium.

Zirconium and niobium were not extracted by ethyl acetate from 0.25*M* quinoline–0.5*M* ammonium thiocyanate solutions at hydrochloric acid concentrations of 0.1 to 6*M*. The mixing time was 10 minutes and equal volumes of the two phases were used.

Table I. Extraction Properties of Zirconium and Niobium with Tri-*n*-butyl Phosphate

Conditions. Carrier-free concentrations of Zr and Nb; aqueous phase, 0.002% oxalic acid, variable HNO_3; mixing time, 35 minutes; volume ratio (org./aq.), 1 to 1

Concn. of HNO_3, *N*	1	2	4	6	10	12
Zr extracted, %	24	40	65	87	93	96
Nb extracted, %	19	25	27	41	63	88

An ethyl acetate solution which was 0.01*M* in 2-nitroso-1-naphthol did not extract zirconium but extracted about 60% of the niobium from equal volumes of aqueous solutions 1 to 8*M* in hydrochloric acid; mixing time was 5 minutes.

Mandelic acid was ineffective in extracting zirconium and niobium out of 0.5*M* sulfuric acid–1*M* ammonium sulfate solutions into amyl alcohol or out of 0.1*M* hydrochloric acid–2*M* sodium chloride solutions into benzene or diethyl ether. The volume of organic phase was twice that of the aqueous phase

and mixing was for 10 minutes. There was, however, partial extraction by amyl alcohol of both zirconium and niobium from an aqueous mandelic acid–0.002*M* oxalic acid solution at a pH of 2.

Neither zirconium nor niobium was extracted in 10 minutes by amyl alcohol or isobutyl acetate 0.2*M* in *m*-nitrobenzoic acid from an equal volume of aqueous solution 0.1*M* in hydrochloric acid and 2*M* in sodium chloride. When tri-*n*-butyl phosphate was used as the solvent containing the *m*-nitrobenzoic acid, about 15 and 5% of zirconium and niobium, respectively, were extracted.

A series of measurements was made of the extraction of carrier-free concentrations of zirconium and niobium by tri-*n*-butyl phosphate from nitric and hydrochloric acid solutions of various concentrations. The extraction of both elements increased as the acid concentrations increased. The behavior was similar with both acids. Results of the studies with nitric acid solutions are given in Table I. Although moderately good extractions can be obtained at the high acid concentrations, separation of the two elements is not feasible under the conditions investigated.

Table II. Extraction of Niobium as a Function of Mono-*n*-butyl Phosphoric Acid Concentration

Conditions. Carrier-free Zr and Nb; aqueous phase, 1*M* HNO_3, 0.004*M* $H_2C_2O_4$, with and without H_2O_2; organic phase, 0.5*M* DBPA[a]; volume ratio (org./aq.), 1:1; 5-minute mixing time

No H_2O_2		3% H_2O_2	
Concn. of MBPA[b] *M*	Nb extracted, %	Concn. of MBPA,[b] *M*	Nb extracted, %
0.47	96	0.47	67
0.18	90	0.18	66
0.13	93	0.13	58
0.11	92	0.11	52
0.003	78	0.003	21
0.0006	75		

[a] Di-*n*-butyl phosphoric acid.
[b] Mono-*n*-butyl phosphoric acid.

The preliminary experiments with the mixed mono- and di-*n*-butyl phosphoric acids indicated good solvent extraction properties for zirconium and niobium. Consequently, more extensive measurements were made.

EXTRACTIONS BY MIXED BUTYL PHOSPHORIC ACIDS

Carrier-Free Concentrations of Zirconium and Niobium. Concentrations of both 0.06 *M* and 0.6 *M* of di-*n*-butyl phosphoric acid in di-*n*-butyl ether were used in these studies. Unless otherwise stated, all experiments in which the concentration of only di-*n*-butyl phosphoric acid is given involved the use of a solution in which the mole ratio of di-*n*-butyl phosphoric acid to mono-*n*-butyl phosphoric acid was 4.5 to 1. All experiments were performed at room temperature; 5 ml. each of organic and aqueous phases were vigorously agitated with a platinum wire stirrer in a glass centrifuge cone. Phases were rapidly and cleanly separated by centrifugation. Mixtures containing known amounts of γ-ray activity of zirconium-95 and of niobium-95 were used. The degree of extraction of each was determined by measuring the total γ-ray activity of each phase and the γ-ray activity of zirconium isolated from the aqueous phase as barium fluozirconate (*2*).

Extraction of zirconium and niobium in carrier-free concentrations by 0.06*M* di-*n*-butyl phosphoric acid from aqueous solutions 1*M* in either nitric, hydrochloric, perchloric, or sulfuric acid and 0.004*M* in oxalic acid was first measured. A single extraction removed at least 99% of the zirconium and left about 98% of the niobium in the aqueous phase. The effect of time of mixing was found to be of importance in the extraction of niobium but not of zirconium. In the case of nitric acid solutions, mixing times of 1, 2, and 5 minutes resulted in extraction of 2, 5, and 10%, respectively, of the niobium; the degree of extraction of zirconium was not influenced by these variations in times. Addition of hydrogen peroxide reduced the extraction of niobium. From aqueous solutions 1*M* in nitric acid, 0.004*M* in oxalic acid, and 3% in hydrogen peroxide, less than 1% of the niobium was removed by the organic phase with mixing periods up to 10 minutes. The behavior of zirconium was unaffected by the presence of hydrogen peroxide.

Measurements of the extraction of carrier-free amounts of zirconium and niobium by 0.6*M* di-*n*-butyl phosphoric acid showed both of them to be efficiently removed. For example, 99% of the zirconium and 95% of the niobium were extracted by 0.6*M* di-*n*-butyl phosphoric acid from a 1*M* nitric acid– 0.004*M* oxalic acid solution; the degree of extraction of niobium was cut to 60% by a 3% concentration of hydrogen peroxide in the aqueous phase. When the zirconium and niobium were in a 1*M* sulfuric acid–2.5*M* ammonium sulfate–0.004*M* oxalic acid solution, 0.6*M* di-*n*-butyl phosphoric acid extracted 99 and 95% of them, respectively. Introduction into such a sulfate solution of hydrogen peroxide reduced the degree of niobium extraction but not that of zirconium; concentrations of 6% hydrogen peroxide reduced the niobium extractions to about 80%.

Information on the role of mono-*n*-butyl phosphoric acid and di-*n*-butyl phosphoric acid in the extraction of zirconium and of niobium is of interest. A series of experiments was performed in which there was measured the degree of extraction of carrier-free niobium by an organic phase of constant di-*n*-butyl phosphoric acid concentration and of variable mono-*n*-butyl phosphoric acid concentrations. The determinations were made with 1*M* nitric acid–0.004*M* oxalic acid solutions both with and without 3% hydrogen peroxide; the organic solvent was 0.5*M* in di-*n*-butyl phosphoric acid, and the concentrations of mono-*n*-butyl phosphoric acid varied from 0.47*M* to 0.0006*M*. The extent of niobium extraction dropped smoothly from 96 to 75% in the absence of hydrogen peroxide and from about 67 to 20% in the presence of 3% hydrogen peroxide. These results are summarized in Table II.

Although the concentration of di-*n*-butyl phosphoric acid seems to be the major factor in the extraction of niobium, it can be seen that mono-*n*-butyl phosphoric acid also plays some part in its extraction.

Similar experiments were performed to study the effect of mono-*n*-butyl phosphoric acid concentrations on the extraction of zirconium. As is shown by Table III, the role of mono-*n*-butyl phosphoric acid is minor in comparison to that of di-*n*-butyl phosphoric acid. Elucidation of the reactions occurring among the constituents of these systems must await more detailed studies.

Table III. Effect of Mono-*n*-butyl Phosphoric Acid Concentration on Extraction of Zirconium

Conditions. Carrier-free Zr and Nb; aqueous phase, 1*M* HNO_3–0.004*M* oxalic acid; volume ratio (org./aq.), 1:1; 5-minute mixing time.

Concn. of DBPA[a], *M*	Concn. of MBPA[b], *M*	Zr Extracted, %	Nb Extracted %
0.5	0.003	99	78
0.05	0.0003	99	1
0.005	0.0011	64	1
0.005	0.00003	45	1

[a] Di-*n*-butyl phosphoric acid.
[b] Mono-*n*-butyl phosphoric acid.

Macro Concentrations of Zirconium and Niobium. The extraction of zirconium and niobium (1 mg. per ml. of each) by the mixed butyl phosphoric acids (mole ratio of di-*n*-butyl phosphoric acid to mono-*n*-butyl phosphoric acid 4.5 to 1) in di-*n*-butyl ether was measured. Exchange between carrier and tracer zirconium and niobium was accomplished by adding hydrofluoric acid (*2*);

sulfuric acid was added and heated to fuming to expel the hydrofluoric acid before the extractions. The solution was made 1*M* in sulfuric acid, 2.5*M* in ammonium sulfate, 6% in hydrogen peroxide, and about 0.004*M* in oxalic acid.

A 15-minute extraction of this solution by an equal volume of 0.06*M* di-*n*-butyl phosphoric acid resulted in more than 99% of the zirconium and 5% of the niobium going into the organic phase. The initial contact of the two phases produced a precipitate at the interface which dissolved upon mixing; the organic phase was pale yellow and the aqueous phase clear. Extraction of niobium was reduced by decreasing the concentration of mono-*n*-butyl phosphoric acid. An organic phase 0.06*M* in di-*n*-butyl phosphoric acid and 0.0003*M* in mono-*n*-butyl phosphoric acid extracted 98% of the zirconium and less than 1% of the niobium with a 15-minute mixing period.

Both zirconium and niobium can be extracted with the more concentrated di-*n*-butyl phosphoric acid solutions. In the absence of hydrogen peroxide 98% of the niobium and more than 99% of the zirconium were removed by a 5-minute extraction. Six per cent hydrogen peroxide reduced the extraction of niobium to about 93%. The organic phase was colored bright yellow in both the presence and absence of hydrogen peroxide; a white precipitate gradually formed in the organic phase as it stood for about an hour.

Table IV. Extraction Properties of Carrier-Free Concentrations of Fission Product Elements with Mixed Butyl Phosphoric Acids

Conditions. Aqueous phase, 1*M* HNO_3, 3% H_2O_2; 5-minute mixing; volume ratio (org./aq.), 1 to 1

Concn. of DBPA[a], *M*	Elements Extracted: <5% by DBPA	5–95% by DBPA	>95% by DBPA
0.06	Cs, Sr, La, Ce (III), Ag,[b] Cd, Ge, Se (IV), Te (IV), Sb (III)[c], Sb (V), As (V), Pd[b], Ru, Rh, Nb	Y 15%, Sn (IV)[b] 50%, Mo[b] 15%	Zr, In
0.6	Cs, Sr, La, Ag[b], Cd, Ge, Se (IV), Te (IV), Sb (III)[c], Sb (V), As (V), Pd[b], Ru, Rh	Mo[b] 23%, Nb 60%, Ta[c] 85%	Zr, Nb[c], Y, In, Sn (IV)[b]

[a] Di-*n*-butyl phosphoric acid solution in which mole ratio of di-*n*-butyl phosphoric acid to mono-*n*-butyl phosphoric acid is 4.5 to 1.
[b] Ag, Sn, Pd, and Mo not carrier-free; their concentrations were 0.5, 3, 8, and 8 γ/ml., respectively.
[c] No hydrogen peroxide present.

Re-extraction of Zirconium and Niobium from Di-*n*-butyl Phosphoric Acid Solutions. Zirconium and niobium were readily removed in either carrier-free or macro amounts from the various di-*n*-butyl phosphoric acid solutions with 4*M* hydrofluoric acid. Saturated oxalic acid solutions gave very slow and incomplete extractions. 2*M* ammonium hydroxide removed zirconium and niobium satisfactorily, but acidification of the solution generated an organic phase which held appreciable quantities of zirconium and niobium.

Extraction Properties of Other Fission Product Elements with Di-*n*-butyl Phosphoric Acid. Studies were made of the extraction characteristics of carrier-free and of macro concentrations of other fission product elements with di-*n*-butyl phosphoric acid. Concentrations of 0.06*M* and 0.6*M* di-*n*-butyl phosphoric acid were used, and the conditions were those employed in isolating zirconium and niobium. Results of the measurements with carrier-free and macro concentrations are given in Table IV and V.

It is apparent that zirconium and niobium can be isolated from each other and from nearly all other fission product elements by extractions with the mixed butyl phosphoric acids.

Separations of Rare Earths with Di-*n*-butyl Phosphoric Acid. It is of considerable interest to note the separation of the yttrium group from the lanthanum group rare earths as effected by 0.6*M* di-*n*-butylphosphoric acid. In carrier concentrations yttrium and holmium are about 95% extracted, while lanthium and cerium are only about 2% extracted. This is a rapid and effective separation method for these rare earths. Further investigations are in progress to determine the extent of separation of other rare earths by this procedure. Application to isolation of individual rare earth elements from all other rare earth elements by multistage extractions are sought.

Table V. Extraction Properties of Macro Quantities of Fission Product Elements with Mixed Butyl Phosphoric Acids

Conditions. Aqueous phase, 1 mg. element per ml., 1*M* H_2SO_4, 2.5*M* $(NH_4)_2SO_4$, 0.004*M* oxalic acid, 6% H_2O_2; volume ratio (org./aq.), 1 to 1; mixing time, 15 minutes with 0.06*M* DBPA and 5 minutes with 0.6*M* DBPA

Concn. of DBPA[a], *M*	Elements Extracted: <5% by DBPA	5–95% by DBPA	>95% by DBPA
0.06	Cs, Sr, Y, La, Ce (III), Ag, Cd, Ge, Se (IV), Te (IV), Sb (III)[b], Sb (V), As (V), Pd, Ru, Rh, Mo, Nb	Sn (IV) 15%, In 85%	Zr, I_2
0.6	Cs, Sr, La, Ce (III), Ag, Cd, Ge, Se (IV), Te (IV), Sb (III)[b], Sb (V), As (V), Pd, Ru, Rh, Mo	Sn (IV) 50%, Ta 35%	Zr, Nb[b], Y, Ho, In, I_2

[a] Di-*n*-butyl phosphoric acid solution in which mole ratio of di-*n*-butyl phosphoric acid to mono-*n*-butyl phosphoric acid is 4.5 to 1.
[b] No hydrogen peroxide present.

Fractionation of Niobium and Tantalum with Di-*n*-butyl Phosphoric Acid. Macro concentrations of niobium were partially separated from tantalum with 0.6*M* di-*n*-butyl phosphoric acid under the conditions indicated in Table V. The effect of concentrations of the several constituents of the system on the degree of separation is being studied in search of conditions for improved separations.

SUMMARY

Of a number of solvent systems examined, that of the mixed butyl phosphoric acids in di-*n*-butyl ether was found most useful for separations of several of the fission product elements.

Conditions for rapidly and efficiently isolating zirconium and niobium from each other and from nearly all other fission product elements have been established; both carrier-free and macro concentrations of the elements can be isolated.

Elements of the yttrium group have been separated from elements of the lanthanum group rare earths with 0.6*M* di-*n*-butyl phosphoric acid in di-*n*-butyl ether.

Partial separation of niobium from tantalum has been attained with 0.6*M* di-*n*-butyl phosphoric acid in di-*n*-butyl ether.

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Spectrographic Determination of Impurities in Zirconium and Hafnium

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Recent developments in the production of zirconium and hafnium have made it necessary to develop methods for determining a large number of trace elements in these materials. This report presents a spectrochemical method for the determination of 22 elements found in zirconium and hafnium metals and oxides. Filings of the metal, or pulverized oxides, are taken and loaded into cratered graphite electrodes. The sample is then volatilized in either an alternating or a direct current arc, depending on elements of interest, and the resulting spectra are photographed and evaluated by conventional techniques. Some of the standards were obtained from the Massachusetts Institute of Technology and the New Brunswick Laboratories of the Atomic Energy Commission; others were synthesized from pure oxides of the base material and analytical grade reagents. Ten parts per million of most of the impurities can be determined with an accuracy of ±30%.

ALL the published spectrographic methods for the analysis of zirconium have been found applicable to the analysis of hafnium. Most of the laboratories associated with this work have even found it possible to utilize the same analytical curves for the analysis of these two materials, because of the unique similarity in the physical, chemical, and excitation characteristics of zirconium and hafnium.

The usual practice is to convert samples to an oxide and utilize some type of direct current arc excitation in order to obtain the desired sensitivity. The impurities are divided into two general categories: the refractories and near-refractories, and the more volatile elements. The latter are usually determined by a method similar to that used in the analysis of uranium—namely, boiling out these impurities by maintaining a temperature in the arc sufficient to vaporize and excite the volatiles but not high enough to excite zirconium and the other refractories. This is accomplished by the addition of some salt, which, in sufficient amount, acts as a carrier and controls the arc temperature in much the same way as any boiling liquid controls the temperature of a solution. Silver chloride, strontium chloride (*9*), and gallium oxide (*8*) are used for this purpose.

A more recent method which obviates the addition of a carrier has been developed by Chandler (*1*). It involves the use of a rotating horseshoe magnet mounted perpendicular to the arc column. The effect here is to propel the electrons around the periphery of the sample electrode, thereby heating the sample and electrode uniformly and maintaining a constant temperature for any given current and analytical gap distance. By adjusting the current to a given temperature just below that necessary to excite the refractories, the volatile elements may be distilled into the arc and determined from the resulting spectrum, which will be relatively free from zirconium background.

With the above-mentioned methods it is necessary to utilize some other type of carrier, such as barium fluoride (*4*), or to burn the sample to completion, in order to determine the near-refractories and refractories. When the oxide samples are burnt to completion, the recorded spectra are erratic and the zirconium background varies in intensity. The spectrum of zirconium is rich in spectral lines, which complicates its interpretation. In order to decrease the intensity of the spectra to a densitometric range, a great deal of sensitivity is lost. Here again the method of Chandler appears to be the most rapid, and probably one of the best. It permits the sample to be excited homogeneously, so that the direct current arc at no time centers on any particular portion of the sample, resulting in a preferential vaporization and excitation of that part. Although this latter method circumvents the recording of erratic spectra, such spectra are still complicated by the excited spectral lines of zirconium.

PRELIMINARY STUDIES

In the preliminary investigations carried out by Westinghouse several of the above-mentioned methods were tried. The carrier salts utilized failed to carry one or more of the desired elements efficiently and reproducibly into the arc stream. Most of this trouble was encountered with the near-refractory elements. In addition, preparation of the sample proved to be time-consuming, as it involved the intimate mixing of weighed amounts of zirconium oxide and carrier salt. The interest was in a high speed method which would furnish results with a precision of ±30% and would not necessitate the building of cumbersome accessory equipment. Jaycox and Ruehle (*6*) mention that in determining calcium, magnesium, aluminum, copper, and iron in zirconium oxide with direct current arc techniques, the results were very poor. However, reproducible results were obtained when a 2000-volt alternating current arc was employed. The authors pointed out that this type of excitation should be of value in analyzing zirconium for other impurities.

Preliminary studies in this laboratory, using 2400-volt alternating current arc techniques in conjunction with standards, soon indicated the validity of Jaycox's suggestion. By proper adjustment of the current and maintenance of the analytical gap it was found possible to record the spectra of the volatiles, near-refractories, and refractories, while the bulk of the zirconium or hafnium remained behind in the sample electrode. The recorded spectra exhibited excellent reproducibility. Moving plate studies (*3*) permitted the selection of optimum circuit parameters for the alternating current arc, adequate exposure periods, and practical sample loads. They also indicated excellent sensitivity and showed the distillation rates of the elements of interest to be far more uniform than with any carrier or straight direct current arc technique. Thus alternating current arc techniques incorporate all the advantages of the above-mentioned methods with none of the disadvantages. This method does not necessitate duplicate recording of the spectra in the same wave length, as do the carrier techniques, in order to obtain the different types of elements. A duplicate wave-length setting must be taken only when values of less than 400 p.p.m. are sought for zirconium in hafnium or vice versa. When lower values are needed, direct current arc techniques have to be used because of the refractory

properties of these elements. This special technique is discussed below.

The investigations were carried out on both a prism and a grating spectrograph. The latter instrument contains a 15,000-line-per-inch grating blazed in the second order. Because of the greater dispersion of this instrument in wave lengths greater than 2600 A., as compared to the prism instrument, there is a greater ratio of signal to noise, resulting in better sensitivity. The total wave-length coverage of the grating instrument is 1300 A., at one setting in the second order. The spectra of the elements whose most sensitive arc lines are below 2600 A. are recorded on the prism instrument, while the elements with their most sensitive spectral lines above 2600 A. are recorded on the grating instrument. This arrangement expedites analysis, because both instruments can be operated simultaneously. It also permits a complete analysis to be made on three 4 × 10 inch photographic plates. When low concentrations of zirconium, hafnium, and lithium are requested, two additional plates have to be exposed, as the special techniques described below are required.

Table I. Spectral Lines

Element	Analytical Line, A.	Concn. Range, P.P.M.
Al	3082.2	20–500
B	2497.7	0.1–20
Ca	3933.7	10–100
Cd	2288.0	0.1–10
Co	3453.5	1.0–100
Cr	3021.6	10–500
Cu	3274.0	1–200
Fe	3021.1	100–1000
Hf	2820.22/2828 Zr[a]	50–20,000
Li	6103.6	10–50
	6707.8	0.5–10
Mg	2802.7	8–200
Mn	2974.8	2–200
Mo	3170.3	5–200
Ni	3002.5	10–500
P	2553.3	10–1000
Pb	2833.1	10–200
Si	2881.6	10–1000
Sn	2840.0	10–200
Ti	3349.0	20–200
V	3185.4	20–300
W	4008.8	10–1000
	2944.4	30–1000
Zr	2844.6/2857.6 Hf[a]	5000–60,000

[a] Internal standard line.

Because most of the samples received by this laboratory are in the metal form, the use of filings for a sample charge was investigated. This method of sampling proved rapid and gave satisfactory results. However, the analytical curves obtained by using filings are steeper than those obtained with oxides. Thus the method for determining the common impurities in zirconium and hafnium consists of the following steps: (1) obtaining filings from the metal samples or pulverizing oxide samples, (2) loading them into cratered graphite electrodes, (3) volatilizing and exciting the samples in an alternating current arc discharge, (4) recording the resulting spectra on a photographic plate, and (5) evaluating them by conventional spectrographic techniques.

RECOMMENDED METHOD

Preparation of Standards. Primary zirconium oxide standards were obtained from the New Brunswick Laboratories and the Massachusetts Institute of Technology. Through cooperation with many of the Atomic Energy Commission laboratories, good agreement was reached on the true values of the added impurities in the standards. Secondary sets of standards were synthesized from pure zirconium oxide and analytical grade reagents. The high purity base material was obtained by precipitating zirconium salt crystals from a chloride solution with sulfuric acid, and converting these crystals to the oxide by igniting them at 800° C. for 1 hour in a platinum crucible. Tertiary standards were then prepared from metal samples. They were first analyzed in the oxide form and the resulting analyses were employed for setting up analytical working curves when filings were used.

The oxide standards are ground in an agate mortar and are then loaded in triplicate into sample electrodes. When metal standards are used, filings are obtained with a hand bastard file. A permanent magnet is passed over the filings four or five times to remove any large amounts of iron contributed by the file. Filing introduces a fairly consistent iron blank of approximately 0.01%. Consequently, for standards or samples containing iron concentrations where this amount is significant to the accuracy desired, millings which have been converted to the oxide must be used. The filings are loaded into sample electrodes in a manner similar to that used for the oxide.

Preparation of Samples. Samples are prepared in exactly the same manner as the standards.

Spectrographs and Accessories. For elements whose most sensitive spectral lines are below 2600 A., a prism spectrograph is used. This includes cadmium, arsenic, boron, and phosphorus.

Hilger Spectrograph. Large quartz and glass instrument
Masks, 0.5-inch mask at the center of the collimating lens; mask with a 4-mm. aperture at the camera
Optics. The source is imaged to the collimating lens by means of a 300-mm. spherical condensing lens placed 20 mm. from the entrance slit of the spectrograph.
Slit setting, 20 microns × 1.5 mm.
Wave-length range, 2200 to 2850 A.
Excitation. Spec-Power source unit, alternating current arc, 2400 volts, 4.85 amperes
Analytical gap, 4 mm.
Prearc period, none
Total arc period, 60 seconds
Electrodes. All electrodes are fabricated from high-purity boron-free graphite rods obtained from the National Carbon Co. Sample is 0.25 inch in diameter and 1.5 inches long with a 1-mm. deep crater containing a center post 0.0625 inch in diameter. Wall thickness is 0.031 inch. Craters are loaded level full. Counter is 0.125 inch in diameter and 1.5 inches long with a 20° cone tip. Water-cooled electrode clamps are used.
Photography. Plates. One 4 × 10 inch Eastman Kodak SA No. 2 plate. Procedures recommended by Eastman Kodak are employed for the development of this photographic plate.
Photometry. Jarrell-Ash comparator microphotometer.
Slit setting, 10 microns × 1.5 mm.
Spectral Lines (Table I). For elements whose most sensitive spectral lines are above 2600 A., the grating spectrograph is used.
Jarrell-Ash spectrograph. 21-foot, second-order grating with 15,000 lines per inch
Masks, 0.5 × 5.25 inch aperture at the collimating mirror for the oxides; 0.25 × 5.25 inch aperture at the collimating mirror for the filings
Optics. The source is imaged to the spectrographic slit by means of a 10-cm. cylindrical quartz lens (axis vertical) in the case of the oxides. No secondary focusing lens is employed when metal filings are arced. The source is projected to the collimating mirror by means of a 45-cm. cylindrical lens (axis horizontal) which is directly in front of the spectrographic slit.
Slit setting, 40 microns × 1.5 mm.
Wave-length setting, 2775 to 4075 A. (second-order)

The excitation, photography, photometry, and selected spectral lines are the same as listed above, except that a total arc period of

Table II. Operation of Card System

(Seidel emulsion number 475,450)

Galvanometer Deflection	Mg, P.P.M.	Galvanometer Deflection	Ti, P.P.M.
21.3	200	22.5	250
28.0	150	27.7	200
34.6	100	35.4	150
37.5	90	39.0	100
41.5	80	43.0	90
45.3	70	46.4	80
51.0	60	50.0	70
56.9	50	54.0	60
64.5	40	59.3	50
74.5	30	65.6	40
86.4	20	73.4	30
93.1	10	78.4	20
94.2	9		
94.6	8		

50 seconds is employed and two SA No. 2 plates are used simultaneously in place of one.

For the determination of low amounts of lithium, the following special conditions are used. (In zirconium and hafnium the lithium content is normally so low that the conditions listed below have to be used when such determinations are requested.)

The grating spectrograph and its settings are exactly the same as those given above, except that the wave-length setting is 5500 to 6800 A. (first-order) and a Corning filter No. 3389 is placed in the external optical path. The photometry and selected spectral lines are also the same

Excitation. Spec-Power source unit, alternating current arc, 4800 volts, 2.4 amperes
Analytical gap, 4 mm.
Prearc period, none
Total arc period, 50 seconds
Electrodes. All electrodes are fabricated from high-purity graphite rods obtained from the National Carbon Co. Sample is 0.25 inch in diameter × 1.5 inches long with a 1-mm. deep crater containing a center post 0.0625 inch in diameter. The wall thickness is 0.031 inch. Craters are loaded level full. Counter is 0.125 inch in diameter × 1.5 inches long with a 20° cone tip. Water-cooled electrode clamps are used.
Photography. Plates. Two 4 × 10 inch III-F Eastman Kodak plates are used.

For the determination of hafnium in zirconium, in amounts less than 0.04%, direct current arc techniques are utilized in conjunction with the grating spectrograph.

Spectrograph and Accessories. Jarrell-Ash, 21-foot, second-order grating with 15,000 lines per inch
Masks, 0.375 × 5.25 inch aperture at the center of the collimating mirror; 50% of the light from the source is utilized.
Optics. The source is imaged to the collimating mirror by means of a 45-cm. cylindrical lens (axis horizontal) placed directly in front of the spectrographic slit.
Slit setting, 40 microns × 1.5 mm.
Wave-length range, 2500 to 3150 A. (second-order)
Excitation. Spec-Power source unit, current direct arc, 220 volts, 16 amperes
Analytical gap, 4 mm.
Prearc period, 5 seconds
Total arc period, 50 seconds
Electrodes. All electrodes are fabricated from regular grade graphite rods obtained from the National Carbon Co. Sample is 0.25 inch in diameter × 1.25 inches long with a 1-mm. deep crater for oxides, 0.25-inch diameter × 1.25 inches long with a 1.25-mm. deep crater containing a 0.0625-inch diameter center post for metal filings. Wall thickness is 0.031 inch in both cases. Craters are loaded level full. Counter is 0.125 inch diameter × 1.5 inches long with a 20° cone tip. Water-cooled electrode clamps are used.
Photography. Plates. One 4 × 10 inch SA No. 2 Eastman Kodak plate is used.

Photometry and spectral line pairs are the same as above, except that background corrections have to be taken into consideration for this type of analysis.

ANALYTICAL CURVES

Densitometric measurements are made on the recommended spectral lines with a microphotometer according to standard

Table III. Precision Evaluation (Zr Metal)

(All values expressed in p.p.m.)

Element	Fe	Si	Al	Cu	Cr	W	Mo	Ni	Ti	Mn	Mg	Pb	Hf
Sample 50482													
Concentration	270	50	30	7	<20	100	<10	20	<20	<5	<8	<30	150
Standard deviation	30	2	10	1	..	20	..	6	..	..	..	..	10
Standard deviation, %	11	4.0	33	15	..	20	..	30	..	..	..	..	6.7
Sample 50635													
Concentration	380	80	50	20	<20	160	<10	30	<20	5	9	30	130
Standard deviation	30	10	10	0	..	10	..	6	..	1	1	10	10
Standard deviation, %	7.9	12.5	20	0	..	6.3	..	20	..	20	11	33	7.7
Sample 50494													
Concentration	650	50	80	7	<20	110	<10	20	20	40	20	70	130
Standard deviation	90	10	10	1	..	10	..	6	4	10	0	4	15
Standard deviation, %	14	20	13	15	..	9.1	..	30	20	25	0	5.7	12

$$\sigma = [(X - \bar{X})^2/n - 1]^{1/2}$$

where σ = standard deviation
X = a separate observation
$\bar{X}$ = arithmetic average of separate observations
n = number of observations

Table IV. Precision Evaluation (ZrO_2)

(All values expressed in p.p.m.)

Element	Fe	Si	Al	Cu	Cr	W	Mo	Ni	Ti	Mn	Mg	Pb	Hf
Sample 22732													
Concentration	140	20	<30	12	<10	180	5.6	14	<10	1.3	<1	<10	120
Standard deviation	32	5	..	1.7	..	20	1.0	3.7	..	0.3	..	..	10
Standard deviation, %	25	25	..	14	..	11	18	26	..	23	..	..	8.3
Sample 204-3													
Concentration	380	120	44	92	<10	450	6.6	30	<10	2.7	1.4	44	120
Standard deviation	70	30	9.5	11	..	50	1.2	5	..	0.7	0.38	11	10
Standard deviation, %	19	27	22	12	..	11	18	17	..	26	27	25	8.3
Sample 235-18													
Concentration	1200	67	81	21	24	98	6.7	6.7	13	37	8.6	210	60
Standard deviation	230	11	10	3	6	3	1.3	1.5	2	6.8	1.3	50	11
Standard deviation, %	19	17	12	14	25	3.1	19	22	15	18	15	24	18

For equation involved, see footnote of Table III.

Table V. Comparison of Results (ZrO_2)

(All values expressed in p.p.m.)

Element	Fe	Si	Al	Cu	Cr	W	Mo	Ni	Ti	Mn	Mg	Pb	Hf
Sample E-500													
Westinghouse	390	21	62	28	19	<30	15	45	10	3	11	<10	110
Other laboratory	300	18	75	23	15	<30	15	45	<10	3.7	9	<10	1300
Deviation	90	3	13	5	3	..	0	0	..	0.7	2	..	20
Deviation, %	30	14	17	22	27	..	0	0	..	23	18	..	15
Sample E-501													
Westinghouse	1200	20	45	11	36	<30	90	7	<10	32	130	90	100
Other laboratory	1300	17	39	10	35	<30	90	6	<10	25	130	100	120
Deviation	100	3	6	1	1	..	0	1	..	7	0	10	20
Deviation, %	7.7	18	15	10	3.0	..	0	17	..	23	0	10	17
Sample E-119													
Westinghouse	2300	230	220	180	130	150	40	270	210	3	<5	10	1600
Other laboratory	2200	190	200	150	130	140	45	250	200	4	<5	<10	1900
Deviation	100	40	20	30	0	10	5	20	10	1	..	..	300
Deviation, %	4.5	21	10	20	0	7.1	11	8.0	5	25	..	..	16

laboratory procedures, and the transmittance values are converted to relative intensities by means of an emulsion calibration curve (*2*). The calibration curve is obtained from a step-sectored spectrogram of iron, and plotted with the galvanometer deflections as a Seidel function (*5, 7*) and the relative exposures as a logarithmic function. (A Seidel function is employed because it gives a nearly straight line between 5 and 95% transmittance values. This results in more accurate analyses when wide ranges of concentration are involved.) For the analytical working curve the three relative intensity values per standard are averaged and the curve is constructed in the conventional manner. No internal standard line is used for any of the elements except in determining hafnium in zirconium and zirconium in hafnium (Table I). This is done in order to simplify calculations and because adequate reproducibility and accuracy could be obtained. For convenience and rapid computation, the working curves can be transferred to the drum of a Dunn-Lowry calculator (*2*). However, to expedite the analyses further, this laboratory has set up a card system, as illustrated in Table II, so that the operator of the microphotometer can record the parts per million of an element directly on the work sheet upon observing the galvanometer reading of that particular element. An average of three determinations per element is reported.

PRECISION AND ACCURACY

Both precision and accuracy were studied. The precision of the analyses for both metal and oxide samples are summarized in Tables III and IV. The material for these tables was compiled over a period of several months and all computations were based on ten determinations for each sample. The results show the precision of the method to be within ±30% of the value reported. As the samples selected for this study came from normal production, a number of the values are reported as "less than." Most of the determinations are reported to only one significant figure. Thus the deviations for some of the values are too large, while others are too small. Nevertheless, the analytical results are of sufficient reliability for the low concentrations involved and they satisfy the requirements of the metallurgist. The determinations at lower concentrations usually show poorer precision. This can only lead to the conclusion that, although the method is designed to produce spectra of equivalent intensity, with background just sufficient to overcome the inertia of the photographic emulsion, the background effects are not completely negligible for low concentrations. Irrespective of this background effect, the precision is satisfactory for practical use. Therefore, the time required to make background corrections is not warranted for routine work.

Table V summarizes the accuracy of this method. As most of the other laboratories use oxide samples, this study was made on oxide samples. The three samples investigated were interchanged with another laboratory; the results indicate that the accuracy is approximately the same as the precision—i.e., ±30% of the value reported. The elements cadmium, boron, phosphorus, lithium, zinc, vanadium, tin, cobalt, and calcium were not included in these studies, because they are present in negligible concentrations and are normally reported as less than a given figure.

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6th Annual Summer Symposium—Less Familiar Elements

Direct Determination of Oxygen in Less Familiar Metal Oxides

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THE determination of combined oxygen in metal and metalloid oxides, and as an impurity in metal salts, is a phase of analytical chemistry which has received relatively little attention. In fact, one of the standard texts on analytical procedures makes the statement, "The determination of combined oxygen is difficult and seldom attempted. It is frequently estimated by difference after determining the other constituents of the substance, after definitely establishing the presence of oxygen" (*6*). The obvious disadvantages of this procedure are that the calculated oxygen content includes the sum of all errors in the other analyses, and requires a complete chemical analysis even when oxygen is the only constituent of interest. The determination of trace oxide impurities in metals and alloys is the one field to which a considerable amount of effort has been directed.

In a few instances the combined oxygen in metal oxides and oxy-acid salts may be determined by their decomposition on ignition—e.g., mercuric oxide, potassium chlorate. Easily reducible oxides (iron, lead, copper, silver, bismuth) may be heated in a hydrogen atmosphere and the liberated water measured. Oxides of molybdenum, tungsten, nickel, and zinc have been analyzed by reaction with sulfur vapor (*3, 10*). The sulfur dioxide produced may then be absorbed by iodate and the liberated iodine determined by titration. Reaction with graphite is probably the most generally applicable procedure. Development in recent years of the vacuum fusion technique has made it possible to determine oxide impurities in many metals, including iron, cobalt, chromium, nickel, titanium, tantalum, manganese, silicon, tungsten, and aluminum, as well as many iron- and aluminum-base alloys.

A procedure for the quantitative determination of oxygen in a number of metal and metalloid oxides has been developed. The method has also been used in the analysis of some oxide solid solutions, mixed oxide phases, ternary oxides, and oxygenated anions, and to determine combined oxygen impurities in some metal salts. The oxygen content of oxide samples (25 to 100 mg.) can be determined with an accuracy of 0.4%. The reagent used, bromine trifluoride, liberates molecular oxygen at 75° C. from oxides of all metals which form volatile fluorides or fluorides soluble in bromine trifluoride.

The method is, in general, applicable only to the determination of oxide impurities in metals, rather than of the oxides themselves, nor can the more volatile metals be analyzed. A number of other methods of more or less general applicability have been developed, especially for oxygen determination in organic compounds, but these are not of concern here.

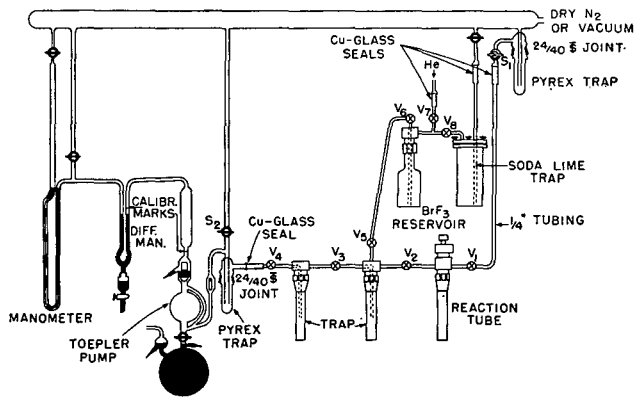


Figure 1. Reaction System

The method discussed involves the reaction of the oxygen-containing compound with the interhalogen, bromine trifluoride. The oxidizing action of this reagent results in the conversion of combined oxygen to free molecular oxygen, which can then be measured tensimetrically:

$$3MO_2 + 4BrF_3 \rightarrow 3MF_4 + 2Br_2 + 3O_2$$

Emeléus and Woolf (*4*) first demonstrated the usefulness of this method in 1950 when they reported on the action of bromine trifluoride on 28 metal oxides. Twelve compounds (CuO, B_2O_3, Tl_2O_3, SiO_2, GeO_2, TiO_2, As_2O_3, Sb_2O_3, SeO_2, UO_3, I_2O_5, and BiOCl) were found to liberate their oxygen completely, while 16 others (BeO, MgO, ZnO, CdO, HgO, CaO, Al_2O_3, CeO_2, SnO_2, PbO, PbO_2, ZrO_2, ThO_2, MnO_2, Fe_2O_3, and V_2O_5) reacted incompletely under the conditions of the experiments. No further information was given as to the extent of this incomplete reaction, except that vanadium pentoxide formed the oxyfluoride, VOF_3. In all other instances the proportions of fluoride and unchanged oxide varied with the experimental conditions and had no special significance. The fact that this work was carried out in a quartz system prevented Emeléus from making any truly quantitative measurements of oxygen evolution, or of subjecting samples to prolonged treatment with bromine trifluoride. Emeléus reports (*7*) that "the loss of weight of the quartz reaction vessel was negligibly small (about 0.01%, a few milligrams on 30 grams) so long as the apparatus was quite dry." These few milligrams would, however, liberate enough oxygen to cause an error of several per cent in the final result, and preclude use of quartz apparatus for a truly quantitative determination. Emeléus concluded from his work that oxides of metals which form volatile fluoride or fluorides which are soluble in the reagent react to liberate their oxygen quantitatively. The authors believe that their modified procedure permits a more nearly quantitative determination of oxygen, and extends its range of usefulness.

PREPARATION AND PROPERTIES OF BROMINE TRIFLUORIDE

Bromine trifluoride is prepared by the direct combination of the elements at or slightly above room temperature (*9*). It is a straw-colored liquid which solidifies at 9° C., boils at 126° C., and has a liquid density of 2.81 grams per ml. at the melting point. Principal impurities which may be present in the compound and their boiling points include bromine (59° C.), bromine monofluoride (20° C.), bromine pentafluoride (40.5° C.), hydrogen fluoride (19.5° C.), and nonvolatile fluorides. It is evident that the trifluoride may readily be purified from these substances by distillation. Although the halogen fluorides are extremely reactive compounds, they may be prepared and purified in copper, iron, aluminum, or nickel equipment.

One of the more interesting properties of bromine trifluoride (and of other halogen fluorides as well) is its high electrical conductivity. At 25° C., the conductivity is 8×10^{-3} ohm^{-1} $cm.^{1-}$ (*2*). Self-ionization occurs by the simultaneous loss and gain of fluoride ions (*11*).

$$2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$$

By analogy with the water system, one may discuss the ease with which a fluoride ion is gained or lost. The addition of antimony, hydrogen, or potassium fluorides to bromine trifluoride changes the ionization equilibrium, since these substances act as acids and bases in this system.

$$SbF_5 + BrF_3 \rightleftharpoons BrF_2^+ + SbF_6^-$$
$$HF + BrF_3 \rightleftharpoons BrF_2^+ + HF_2^-$$
$$KF + BrF_3 \rightleftharpoons K^+ + BrF_4^-$$

Bromine trifluoride acts as an acid in bromine pentafluoride, and the pentafluoride is a base in the trifluoride

$$BrF_3 + BrF_5 \rightleftharpoons BrF_4^+ + BrF_4^-$$

As might be expected, a mixture of these two shows an acid strength intermediate between the two pure compounds.

Whereas the action of bromine trifluoride on metals is closely related to ionization and concentration of cations in solution, its reactivity toward metal oxides is of a different nature. One possible explanation involves a metathesis reaction to form the metal fluoride and bromine oxide or oxyfluoride, followed by decomposition of the bromine oxide to give molecular oxygen as one of the products.

Bromine trifluoride has several advantages over other reagents which might be considered for oxygen analyses. It has a relatively high boiling point, thus permitting liquid-phase reactions over a convenient temperature range; in this respect it is to be preferred to fluorine gas, bromine pentafluoride, or chlorine trifluoride. It can readily be prepared free of any oxygen-containing impurities, whereas tank fluorine usually contains small amounts of oxygen which are difficult to remove. No thermally

stable bromine oxides are formed. Chlorine trifluoride forms chlorine oxides which are stable at 300° to 400° C and require an electric discharge to effect their decomposition.

No evidence has been found for the formation of oxides of fluorine in any bromine trifluoride reaction with metal oxides.

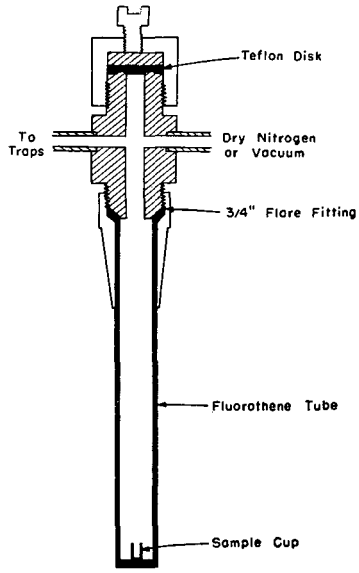


Figure 2. Cross Section of Reaction Tube

EQUIPMENT

The apparatus (Figure 1) may be said to consist of two portions—the reaction system which is exposed to the corrosive fluorine compounds, and the collecting and measuring system for the liberated oxygen.

The reaction system is constructed entirely of nickel and the fluorine-inert plastics Fluorothene (polychlorotrifluoroethylene) and Teflon (polytetrafluoroethylene), except for the soda-lime trap, which is brass. The system includes a bromine trifluoride reservoir (100-ml. volume), a soda-lime trap through which the reservoir may be evacuated, a Fluorothene reaction tube (Figure 2), and two Fluorothene traps. The Fluorothene tubes are drilled from rodding 1 inch in diameter (internal dimensions, $^6/_8 \times 5^1/_2$ inches; external dimensions, $^3/_4 \times 6$ inches). A vacuum-tight connection to the machined nickel head is made with a $^3/_4$-inch SAE flare nut. The tubing which connects the components is of $^1/_4$-inch nickel, and the valves are Hoke Inconel diaphragm valves. The borosilicate glass portion of the apparatus includes a removable trap at either end of the reaction system, an automatic Toepler pump to collect the liberated oxygen, a calibrated volume with a differential mercury manometer to make it a constant volume system, and a standard vacuum mercury manometer. The apparatus is connected at either end and at the junction of the two portions to a high vacuum manifold.

PROCEDURE

Bromine trifluoride is forced from the reservoir into the tubing between V_5 and V_6 (volume 7 to 8 ml.) with helium. The reagent is then admitted to the reaction system through V_5 and a portion of the liquid is distilled into each tube to prefluorinate the apparatus completely. The heat source which has been found convenient for all distillations is a hair dryer. At ~75° C. the bromine trifluoride can be moved from one tube to another in 15 to 20 minutes. After no more noncondensable gas is produced on further heating, the system is thoroughly evacuated, all the trifluoride is distilled into the reaction tube cooled by a liquid nitrogen bath, and V_2 is closed.

V_1 and V_4 should never be opened without first cooling both the adjacent borosilicate glass trap and Fluorothene tube to liquid nitrogen temperature. The glass traps were found necessary to prevent diffusion of mercury vapor into the reaction system, where it reacts with bromine trifluoride to form slightly volatile mercurous fluoride. They also prevent contamination of the glass vacuum line with traces of slightly volatile fluorides which have not condensed in the Fluorothene tubes.

Nitrogen gas which has been dried by passing through a phosphorus pentoxide column and a trap cooled with liquid nitrogen is admitted to the reaction tube through V_1 at a pressure of about 850 mm. The screw cap of the tube may then be removed to permit addition of the substance being analyzed. The slow stream of nitrogen emerging from the head of the tube effectively prevents the entry of water vapor. The sample (25 to 125 mg.), which has been weighed into a small Teflon cup, is then dropped into the reaction tube, and the cap is quickly replaced. The system is thoroughly evacuated and V_1 is closed. The reaction tube is then heated at 75° C. for 2 hours. Oxygen evolution usually begins when liquid bromine trifluoride comes in contact with the oxide; in a few instances the reaction is violent enough to cause flaming. Dissolution of the sample is complete within a few minutes, but the longer heating time is necessary to decompose any bromine oxide or oxyfluoride formed as an intermediate.

To measure the oxygen evolved, the reaction tube is cooled to room temperature, the Fluorothene traps are cooled to liquid nitrogen temperature, S_2 is closed, and V_2 is opened. The liberated oxygen is pumped (Toepler) into the calibrated volume while the other volatile reaction products are trapped out. The differential manometer may be balanced by admitting nitrogen through the manifold. The volume of the authors' calibrated system (~33 cc.) gives best results with oxygen samples measuring 10 to 15 cc., but the volume may be adjusted over a large range to fit varying needs.

A blank run using the procedure outlined above gave no measurable quantity of noncondensable gas. A series of nine reproducibility runs on a single oxide sample showed an average deviation of 0.40%, with a maximum deviation slightly greater than 1%.

Replacement of the reaction tube and removal of reaction products from the reagent are accomplished simultaneously. All the volatile materials, including bromine trifluoride, are first condensed in the traps, after which they are permitted to warm to room temperature. A liquid nitrogen bath is then placed on the reaction tube. The more volatile products are allowed to condense in the reaction tube, during which time very little of the trifluoride will distill. V_2 is then closed, dry nitrogen is admitted to the tube through V_1, and the tube is replaced by a clean tube, which is then evacuated and prefluorinated as described above.

MATERIALS

The bromine trifluoride used for these experiments was obtained from the Harshaw Chemical Co. It was purified by distillation in an all-nickel still under reduced pressure; the fraction boiling at 95–95.5° C. at 250 mm. was used. The uranium compounds were prepared as described in Table I, and the titanium monoxide samples were obtained from P. W. Gilles, University of Kansas, and were treated with bromine trifluoride as received. The remaining compounds investigated were re-

Table I. Oxygen Analyses of Uranium Oxides

Sample No.	Nominal Composition	Method of Preparation	Theoretical Oxygen Obtained, %[a]
1	UO_2	Hydrogen reduction of UO_3 at 750° C.	101.0
2	U_3O_8	Air ignition of $(NH_4)_2U_2O_7$ at 750° C.	100.0
3	UO_3 (phase III)	Oxidation of U_3O_8 at 500° C., 50 atm. O_2	99.9
4	$UO_{2.41}$	$UO_2 + U_3O_8$ mixture ignited one week at 1200° C. in evacuated tube	100.0
5	$UO_{2.55}$		100.0
6	$UO_{2.60}$		99.5
7	48.4% MgO–51.6% UO_2	Mixed oxides heated to 1600° C. in H_2	68.5
8	$MgUO_4$	$MgUO_2(SO_4)_2$ ignited to 1100° C. in air	100.0
9	70% ThO_2–30% UO_2	Ignition of mixed oxides at 1500° C. in H_2	1.3
10	50% ThO_2–50% UO_2		5.1
11	30% ThO_2–70% UO_2		76.4
			84.0 (4 hours)
			95.0 (20 hours)
12	10% ThO_2–90% UO_2		100.7

[a] All heating times are 2 hours except where noted.

Table II. Titanium-Oxygen Ratios from Titanium Oxide Sublimation Studies

	Sample	Calculated Composition
1	Original material	$TiO_{0.99}$
2	Residue, 8% sublimed	$TiO_{1.01}$
3	Residue, 13.65% sublimed	$TiO_{1.04}$
4	Residue, 27.5% sublimed	$TiO_{1.14}$
5	Sublimate	$TiO_{0.85}$

Table III. Oxygen Analyses of Metal Oxides and Salts

No.	Reactant	Reactivity[a]	Theo. O Obtained, %	Comments
1	TiO_2	++	99.1	TiF_4
2	GeO_2	++	101.2	GeF_4
3	CeO_2	−	5.2	10.7% reacted in 6 hours. CeF_4 may be slightly soluble
4	PbO	+	98.1	Slow reaction may require longer heating period
5	PbO_2	+	99.5	PbF_4
6	V_2O_5	++,+	96.9	Contained traces of lower oxides, VOF_3 is intermediate
7	Nb_2O_5	++	101.4	NbF_5
8	Ta_2O_5	++	100.0	TaF_5
9	Cr_2O_3	+	99.1	Green CrF_3 precipitated
10	$K_2Cr_2O_7$	++,+	99.4	Green CrF_3 precipitated
11	MoO_3	+	65.9	$MoOF_4$ is stable intermediate
12	TeO_2	++	107.0	Impure sample, contained 3% SiO_2 plus other trace impurities
13	TeO_2	++	100.0	Recrystallized from dilute HNO_3
14	WO_3	++	101.4	WF_6
15	MnO_2	−	0.5	
16	$KMnO_4$	+	99.9	Red fluoride formed (MnF_3?)
17	$KReO_4$	+	49.4	$ReO_3F_4^-$ is stable intermediate
18	$BiPO_4$	++	100.1	$BiF_3 + PF_5$
19	$BaSO_4$	+	25.1	Emeléus (*4*) reports formation of $(SO_3F)^-$ ion
20	$BaBr_2.2H_2O$	++	101.9	$BaF_2 + HF$

[a] ++ moderate reaction, + slow reaction, − little or no reaction.

agent grade chemicals (Merck, Baker and Adamson, Fansteel, or Mallinckrodt) with the following exceptions: vanadium pentoxide and tellurium dioxide were from the Fisher Scientific Co., cerium oxide was from the G. Frederick Smith Co., potassium perrhenate (99.5% pure) was from the Department of Chemistry, University of Tennessee, and germanium oxide, tungsten oxide, bismuth phosphate were laboratory preparations.

RESULTS

Results to date are reported on a number of binary and ternary oxides, oxy-acid salts, solid solutions, mixed oxide phases, hydrates, and compounds containing combined oxygen as an impurity. The majority of the metal oxides listed are those of the less familiar elements.

Uranium Oxide. The metal-oxygen system most thoroughly investigated is the uranium-oxygen system. Some of the results obtained are tabulated in Table I. Samples 1 to 3 were pure oxides. The high result obtained on the dioxide is in agreement with the observation of Roberts (*5*), that surface oxidation of the powdered oxide occurs at room temperature to give a composition approximately $UO_{2.02}$. Samples 4 to 6 were mixtures of $UO_{2.02}$ and $UO_{2.67}$ being used to study the phase relationships in the system between O/U = 2.25 and 2.67. Sample 7, containing two crystalline phases, one of which (MgO) is inert toward bromine trifluoride, liberated only the oxygen associated with the uranium oxide. Combination of these same constituents into the ternary oxide, $MgUO_4$, resulted in complete reaction. Samples 9 to 12 constitute a comparison of the reactivity of an oxide solid solution, one component of which (ThO_2) does not react with bromine trifluoride. It is evident that thorium dioxide effectively prevents liberation of the oxygen until it becomes a minor constituent of the solid solution. When reaction does occur, the oxygen associated with both components is evolved.

The bromine trifluoride method has also been used to determine combined oxygen impurities in uranium tetrafluoride. A sample of the tetrafluoride to be used for low temperature heat capacities by Lohr and Osborne at this laboratory was found to contain 0.3% combined oxygen. A vacuum sublimation at 1050° C. reduced the oxygen content to 0.1%, and a second sublimation at 1000° C. further decreased the oxygen to 0.005%.

Titanium Monoxide. A group of five titanium monoxide samples were provided by P. W. Gilles, Department of Chemistry, University of Kansas. These were selected from samples obtained in an investigation of the heat of sublimation of this oxide. Results (Table II) indicate that stoichiometric titanium monoxide is not sublimed; the sublimate is titanium-rich, leaving a residue with progressively greater oxygen content as the volatilization proceeds.

Other Oxides. The results of analyses to date on a number of oxides, oxy-acid salts, and hydrates are reported in Table III. There is agreement with the reported results of Emeléus and Woolf (*4*) in all but three instances. Both lead monoxide and lead dioxide were found to have reacted almost completely after 2 hours at 75° C., and the vanadium oxyfluoride reported by Emeléus was found to have been almost completely decomposed by bromine trifluoride under the condition of the experiment. Two compounds were found, however, which did form oxyfluorides—molybdenum trioxide reacted to form $MoOF_4$, and potassium perrhenate gave an oxygenated compound, possibly $KReO_2F_4$, containing half of the oxygen originally present.

DISCUSSION

The results reported here indicate clearly that the oxygen content of a considerable number of metal oxides and oxy-acid salts can be determined accurately by the bromine trifluoride method. The method can also be useful for determining combined oxygen impurities in certain metals or metal salts, and may find some use in determining degree of hydration of metal salts. The range of applicability of the method, which had been outlined to a considerable extent by Emeléus and his coworkers, has been defined further. A modified periodic table (Figure 3), gives an over-all picture of the reactivity of bromine trifluoride toward oxides and oxy-acid salts.

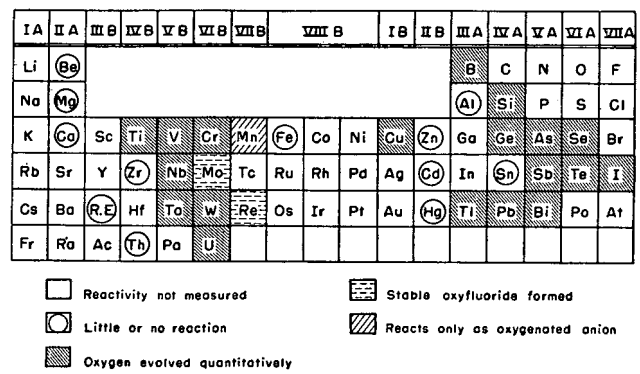


Figure 3. Reactivity of Oxides with Bromine Trifluoride

As compiled from Emeleus and Woolf (*4*, *11*) and this work

From a thermodynamic standpoint all metal oxides should react with bromine trifluoride to form the metal fluoride and liberate oxygen. In practice this is not achieved, possibly because of a high activation energy for the reaction, or because an insoluble metal fluoride film protects the bulk of the oxide sample from the reagent. A recent study of the solubility of metal fluorides by Sheft, Hyman, and Katz (*8*) enables one to make predictions concerning the reactivity of oxides which have not been investigated as yet. They find an appreciable solubility of alkali metal fluorides in bromine trifluoride, which is attributed to the ability of bromine trifluoride to accept a fluoride ion to form the BrF_4^- grouping. Progressive decrease in solubility of metal fluorides in going from Group I to Group IV is believed to be due to the increasing charge on the metal ion, which results in a decrease in tendency to give up fluoride ions. As one proceeds beyond Group IV, the ability of bromine trifluoride to act as a fluoride ion donor as well as acceptor results in increased metal fluoride solubility due to the formation of salts of the type $BrF_2^+MF_6^-$. On the basis of these observations, it may be predicted that the

alkali metal oxides as well as the heavy alkaline earth oxides will react with bromine trifluoride, but that the Group III and IV oxides will be inert, except for those metals which form volatile fluorides.

Several metal oxides which form insoluble, nonvolatile fluorides react with bromine trifluoride. Whether this reactivity is due to the formation of a nonadherent fluoride film, or to some other cause, has not been determined.

A number of possible changes in procedure are possible in an attempt to increase the number of metal oxides that can be analyzed. Some qualitative experiments reported by Andrews and Katz (*1*) indicate that beryllium, mercuric, ceric, zirconium, manganese(IV), cobaltic, and nickel oxides can be completely converted to the fluorides by bromine trifluoride at 300° C. in a high-pressure vessel. No attempt was made to measure oxygen evolution and the extent of reaction was calculated from weight change and crystal structures. A mixed bromine trifluoride–hydrogen fluoride reagent caused complete fluorination of aluminum, lanthanum, and calcium oxides at 200° C. Modification of equipment to permit collection of oxygen generated by high pressure, high temperature exposure to bromine trifluoride would materially increase the number of oxides which can be analyzed.

The authors' work to date has been concerned principally with obtaining a quantitative evolution of oxygen from oxide samples, and very little with reaction mechanisms, or characterization of final products or of intermediate products when they appear. They hope to investigate these fields as well as the reactions of bromine trifluoride with a number of other groups of compounds including nitrides, carbides, and borides.

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6th Annual Summer Symposium—Less Familiar Elements

Present Limitations of Platinum Group Analysis

Introduction to the Symposium on the Platinum Metals

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THE analytical chemistry of the platinum group metals (osmium, rubidium, palladium, platinum, rhodium, and iridium) was thoroughly reviewed in 1943 by Gilchrist (*2*) of the National Bureau of Standards. He observed that the extensive literature was difficult to organize except under individual authors because there was often little relationship between ideas from different laboratories. Consequently the description of the analytical chemistry of the platinum group metals under a few general chemical reactions is inadequate. He did, however, point out that the problems of platinum group analytical chemistry can be grouped under the headings: (1) solution of ores and metals, (2) separation of platinum group metals from other metals, and (3) separation of platinum group metals from each other. To this must be added a fourth, determination of platinum group metals.

The trend of research in platinum group chemistry since the appearance of the Gilchrist review in 1943 is indicated by the distribution in subject matter of papers shown in Table I. The trend in all this work has been toward specific methods for detection and determination, without the necessity for separation if possible. Methods used have been largely empirical, so that little conclusion can be drawn as to the specific properties involved.

During the period 1900 to the present, platinum group analysis has been of prime interest in connection with the development of Canadian ores. At Toronto University, Beamish (*1*) and his coworkers have been concerned with the dissolving of ores and metals containing platinum group metals and with separations and determinations of individual metals. Their experience is summarized in the first paper of this symposium.

A widely used method of analysis for mixtures of platinum group metals is that of Gilchrist and Wichers (*3*) of the Bureau of Standards, published in 1935. The unique experience of the Bureau of Standards in applying these methods over a 20-year period is represented in the paper by Raleigh Gilchrist.

Among the newer developments in platinum group chemistry are the measurement and evaluation of specific properties of platinum group metal compounds which are useful in analysis. The photometric study of complex ions, their formation and stability, and subsequent use in analysis is the subject of the paper by Gilbert Ayres of the University of Texas.

Although there has been a trend toward discovery of specific reagents for detection and determination for strictly analytical purposes, there have also occurred an increased interest in and need for quantitative separations of the platinum group metals.

Table I. Publications on Platinum Group Chemistry, 1943 to 1952

Subject	Number of Publications
Solution of samples	3
Qualitative detection	10
Separations	
Chromatography (column)	10
Chromatography (paper)	2
Electrolysis	8
Extraction	1
Fluxing	2
Organic reagents	120
Volatilization	7
Wet inorganic methods	65
Zinc sulfide column	5
Determinations	
Colorimetry	38
Fluorophotometry	3
Gravimetric methods	10
Polarographic	3
Potentiometric titration	16
Spectrographic	38
Volumetric methods	9
X-ray diffraction	18
X-ray fluorescence	2

Methods of separation are naturally important in the industrial preparation of these metals. Radiochemistry has emphasized the need for chemical separations of these metals. It has also placed a special demand—that of speed—upon the chemist concerned with the operations of solution and separation. An unusual example of difficulty occurring in radiochemistry, in the author's laboratory, is the greatly increased resistance to chemical attack of iridium which has been bombarded in the cyclotron. Consequently it becomes necessary to look for more rapid chemical methods. The fourth and last paper of the symposium is concerned with separation by means of ion exchange resins.

The principal limitation in platinum group analysis at present therefore is that the methods, excellent as they are as to results, are too slow to fit the needs of radiochemistry. More rapid methods of quantitative separation are especially needed. Platinum group chemistry has also been largely empirical. Systematic quantitative studies of solubilities of precipitates, of adsorption phenomena, of complex formation and stability, of photometric behavior, and of electrochemical behavior are needed. The systematic application of such information should lead to an improved analytical scheme for the platinum group metals.

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6th Annual Summer Symposium—Less Familiar Elements

Concentrating and Dissolving Platinum Metals

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This is an interim report of the efficiency of the fire assay for ruthenium, osmium, rhodium, and iridium. Reference is made to the losses caused by cupellation and to the methods of effecting quantitative corrosion of platinum metals and their alloys. Data are provided to prove that certain types of fluxes may "slag off" some of the platinum metals. Of particular significance is the fact that prefusion of ore mixtures may result in very unsatisfactory assay recoveries. This observation suggests the possibility that similar phenomena may be found in natural occurrences. Furthermore, these researches provide the first experimental data on the efficiency of lead collection.

THE treatments which go to make up the fire assay for precious metals go back a great many years. In discussing the history of assaying, Smith (*17*) mentions that many of the procedures such as cupellation and parting are recorded as early as the 12th or 14th century. The refining of silver by fire in the manner of cupellation is recorded by Jeremiah in the Old Testament.

The operations are by no means well known to many chemists. At universities, assaying is taught in schools of mines or of mining engineering, and the average chemistry student hears very little or nothing about it. Nevertheless, the operations involved when an assay is required for the platinum metals call for a high degree of chemical skill. Thus, Bugbee (*7*) states, in connection with the platinum metals, "their correct determination is considered the most difficult analysis in the realm of inorganic chemistry."

The success of the crucible assay depends on several factors. One is having the ore reduced to a very fine powder and intimately mixed with the flux. The choice of composition for the flux is governed by the composition of the gangue to be slagged off. For instance, an ore rich in silica requires a compensating amount of soda ash and litharge to form a suitable slag. The composition of the flux and the temperature of the furnace must be controlled so that reduction of lead occurs while the slag is still quite viscous. In this way the extraction of the precious metal occurs throughout the body of the charge. Later, the temperature may be raised, and as the slag becomes more fluid the minute droplets of lead fall and collect together in the base of the crucible.

Some knowledge of the approximate composition of the gangue is necessary to predict the amounts of acidic or basic oxides to be added in order to form a suitable slag and to predict the amount of reduction of litharge which may take place by the action of sulfides. The characteristics of a good slag are numerous. It should remain rather viscous early in the fusion while the lead drops are forming, but become more fluid at somewhat higher temperatures; it should separate cleanly from the lead button after cooling; and its composition must not be so basic as to corrode out the clay crucible.

Ideally, about 25 grams of lead should be produced and form the so-called button on cooling. For ores containing but little sulfide, the quantity of lead in the button is regulated by the amount of flour or other reducing agent added with the charge. Sulfide ores themselves will reduce litharge, and it is customary to express the reducing power of an ore as the number of grams of lead produced by the reducing action of 1 gram of ore. Since it is desired to limit the size of the buttons and also to leave some unreduced litharge in the slag, the custom is to add potassium nitrate as an oxidizing agent in the assay of sulfide ores; this is the so-called niter assay. Another practice, somewhat rarer and certainly more time-consuming than the foregoing, is to roast the ore with free access of air in order to convert sulfides to oxides.

Mention should also be made of the iron nail assay. In this method, the reduction of litharge is accomplished by an excess of iron, usually in the form of nails. These are removed before the melt is poured. This type of assay is applied to sulfide ores and usually gives rise to a ferrous sulfide matte. With this treatment a large amount of soda ash is added to the flux and much of the iron matte dissolves in the slag in the form of sodium ferrous sulfide. A large proportion of base metals is found in the button in the case of the iron nail assay. The contents of the crucible or pot are poured into a conical mold, and on cooling the slag breaks away or can be removed from the lead button.

The scorification assay consists of heating together ore and lead, plus a small amount of borax, in an oxidizing atmosphere. This is carried out in a muffle furnace on a shallow saucerlike

dish. The lead is partially oxidized to litharge which exerts a solvent action on the silica and other dross of the ore, while the remainder of the lead collects the precious metals in a button. Any sulfides are first oxidized, and the resulting oxides form solid solutions with litharge. The scorification method finds principal application in the assay of silver and rich gold ores, but it is also of interest in platinum-metal work where scrap, sweepings, and the like are to be treated for the concentration of precious metals.

CUPELLATION

The two preceding operations are customarily followed by cupellation. Cupels are small thick cups, generally made of bone ash or similarly porous materials. The button from the fusion treatment is placed on the previously heated cupel and heated in a muffle furnace with free access of air. The lead oxidizes to litharge which, at the temperature of its formation, is a liquid; some of this vaporizes, but most of it soaks into the porous cupel. While the molten litharge wets the cupel and runs into the interstices of the bone ash, the remaining lead alloy has a higher surface tension and stays as a globule on the surface. The litharge here acts, as in the scorification assay, as a solvent for oxides of base metals. Gold, platinum, and probably silver are not oxidized while the other platinum metals may form oxides. The precious metals or their oxides eventually remain as a bead on the cupel after the lead has all been consumed. Usually a known weight of silver is added to the ore or the button so that the bead is of a convenient size and, much more important, gives a proper parting when treated with acid.

The procedures just described have been used for a very long time in the analysis of ores for gold and silver. Errors have been encountered, especially a loss of silver during cupellation. This is considered to be due mainly to the formation of oxide which is dissolved and absorbed with the litharge. Quantitative data for this loss are available but hard to interpret owing to the failure of many experimenters to control their conditions with sufficient care. It is known that the losses are greater the higher the temperature during cupellation and also the greater the amount of lead in the button.

POSSIBLE LOSSES OF PLATINUM METALS

Similar quantitative data have not been available for the platinum metals and the assumption appears to have been generally made that, with minor modifications, the procedures long in use for the gold assay up to the parting of the bead will yield satisfactory results for platinum and its congeners. This assumption cannot be entirely warranted because of several features of the chemistry of these metals.

In the first place, the platinum metals are much more disposed to form oxides than gold or silver. The characteristic inertness of these elements to surface corrosion and oxidation tends to obscure the fact that they are thermodynamically much more active than silver or gold. Latimer (*13*) has given some values for the standard free energies of formation of some of the oxides (Table I).

While these data are in some cases only estimates and do not permit any calculation of equilibrium constants at the higher temperatures characteristic of furnace work, they do indicate that there is a greater tendency to oxide formation than is sometimes thought. For this reason, the possibility must be considered of these metals being retained in solution as silicates or borates in the slag during the crucible assay. Likewise, an even more appreciable loss may occur in cupellation with the dissolving of platinum metal oxides in the molten litharge.

It is also known that two of the platinum metals form volatile oxides of known composition, and the existence of gaseous oxides has also been postulated to account for the small loss in weight that occurs when platinum, palladium, or iridium are heated in air. Loss of these metals during certain furnace treatments may therefore be anticipated. This may be especially true in the latter stages of cupellation because the melting points of the final beads are much higher when they contain platinum metals than when they contain gold and silver only.

Cupellation losses are known to occur with gold assays, especially if the temperature becomes too high or if the proportion of silver in the final bead is too low. This seems to be mainly a mechanical loss, perhaps arising from a lowering of the surface tension of the alloy under these conditions. When the platinum metals are considered, a further source of mechanical loss may be expected because of the insolubility of rhodium and iridium and the restricted solubility of platinum in silver. The presence of iridium seems particularly apt to cause precious metal to be left behind on the cupel in a finely divided state.

EXPERIMENTAL WORK ON FIRE ASSAY

A thorough-going investigation of the efficiency of these fire-assay techniques when applied to platiniferous ores and concentrates has been in progress in this laboratory over a period of years. Results of this study have now been published for ruthenium (*18*), osmium (*1*), rhodium (*3*), and iridium (*6*). Examination of the distribution of palladium and platinum during these treatments is in progress.

There is a considerable body of evidence or opinion that the most serious losses of platinum metals occur during cupellation, probably for the reasons outlined above, and these losses in cupellation have been verified. Accordingly a composite method of analysis for the platinum metals is being worked out based on dissolving or parting of the lead button. This has introduced a few analytical complications, but it seems probable that button parting will be required in the future for precision work.

Procedure. The procedure in these investigations has been approximately the same for each of the metals investigated. Synthetic or naturally occurring ores of different types were salted with known amounts of the platinum metal. The salting technique was either by direct addition of weighed amounts of sponge metal or by addition of known amounts of standard solution followed by drying. The ore samples used always included a siliceous (nonreducing) and a sulfide (reducing) type.

The ore samples were mixed with various types of fluxes, acidic, neutral, or basic, and fused in the crucible assay. Different procedures for the assay of the sulfide ores were tried: preroasting of the sample and the niter assay in all cases and the iron nail assay in the study of ruthenium and of osmium. The buttons resulting were analyzed for the precious metal directly. In this connection perchloric acid parting proved of great use, especially in ruthenium and osmium analyses. The slag from the first fusion was all collected, ground fine, and re-fused with litharge and flour to give a second button. In extreme cases, as the analysis required, further reassaying of the slag was continued until the platinum metal was reasonably well accounted for. In the cases of ruthenium and osmium the gases over the fusion mixture were aspirated from the crucible through suitable absorbing solutions. The latter were then analyzed for the appropriate metal.

In three of the four researches thus far reported (all but rhodium) the loss of platinum metal during cupellation was examined. This examination required collecting and analyzing vapors given off in the case of ruthenium and osmium and also an assay of the ground cupel after the bead had been removed. In all cases the beads were analyzed for the metal.

Ruthenium analyses were performed by thionalid precipitation

Table I. Standard Free Energy of Formation of Noble Metal Oxides

Oxide	$F°$, Kcal.
Ag_2O	−2.6
Au_2O_3	39.0
PdO	−14.4
PtO	
RhO	−16.0
Rh_2O_3	−50.0
Ir_2O_3	−42.0 (estimated)
RuO_2	−40.7
RuO_4	−33 (estimated)
OsO_4	−67.9

(*15*) and by counting of radioactivity; the two procedures enabled cross checking in the case of large samples and the radioactive counting enabled quick estimation of small amounts of ruthenium in vapors and filtrates. Osmium analyses were all performed colorimetrically by means of thiourea (*2*, *4*). It was found that the distillation procedure introduced considerable and variable amounts of silica into the sample which precluded the use of gravimetric analysis.

Rhodium was determined after precipitation with thiobarbituric acid (*3*). This reagent was applied to chloride solutions and had the advantage that lead in moderate amounts could be tolerated in solution during the precipitation. When a double precipitation of rhodium was carried out, results of great accuracy were obtained for rhodium in the presence of 10 grams of lead. Rhodium was first isolated from large amounts of lead by treatment of the solution with zinc. The small amounts of lead carried down by the zinc were not precipitated by thiobarbituric acid.

Iridium analyses were carried out on the residues from nitric acid or perchloric acid parting of the lead button. A short procedure consisted of treating the ignited residue repeatedly with sulfuric acid and hydrofluoric acid to remove silica and subjecting the final residue to leaching with dilute nitric and hydrochloric acids in succession. Other residues were treated by hot chlorination on a bed of sodium chloride to render the iridium soluble (*10*). Base metals and silica were then removed by precipitation with phosphate in the presence of sodium nitrite, and finally the iridium was determined hydrolytically (*5*).

Results. The results of these investigations are very interesting. It was found, for instance, that neither ruthenium nor iridium was completely collected into the lead in one fusion. One additional fusion with litharge and flour sufficed to extract the remainder of the ruthenium, but at least two extra fusions were required in the case of iridium. Recovery of ruthenium in the first fusion was found to be from 75 to 95% on a 6-mg. sample, and no difference could be found among the slag losses for acidic, basic, or neutral fluxes.

The distribution of iridium was more exhaustively studied. The first fusion extracted about 90% of a 5-mg. sample when various fluxes were used. With acidic or neutral slags, the remainder of the iridium was recovered in two reassays, but more than 5% of a 5-mg. sample was lost when basic slags were used. Even more startling losses were recorded when the assay was attempted on copper sulfide or nickel oxide ores. These required a basic flux with excess litharge for slagging, and the loss of iridium in these assays was from 20 to over 60%. Furthermore, copper and nickel always appeared in the lead button in these cases.

The failure to recover ruthenium or iridium in one fusion is thought to be due, in part at least, to limited solubility of these metals in lead. The loss of iridium to basic slags is a much more subtle phenomenon. It appears necessary to postulate that iridium forms a compound with some of the constituents in the flux, and as the observation is confined to basic slags, this suggests the formation of an acidic oxide of iridium. The presence of iridium in the slag could not be proved by spectrographic examination. If a flux salted with iridium were fused without button formation, and then assayed and reassayed the total recovery of iridium was less than 80%. There is evidence that this phenomenon is not confined to iridium.

Rhodium and osmium gave much more satisfactory assays. Data on rhodium are the least complete, but they reveal that on one fusion, plus a reassay of the slag, recovery of 10 mg. of metal was of the order of 97 to 99% complete. Collection in the first button was of the order of 94 to 98% irrespective of the ore type and flux used. Nickel oxide ores gave slightly poorer recovery in the first button.

The study of the distribution of osmium was very complete and disclosed that the efficiency of the assay depended somewhat on the type of flux used. The best collection seemed to be obtained with neutral fluxes and was of the order of 96 to 99%. Moreover, in these cases the collection was virtually complete in the first button. A representative acid flux of medium viscosity yielded poor collection in one button; at least two reassays of the slag were required to make the collection nearly complete, and gas losses were appreciable in every fusion. A different acid flux, rich in borax and quite fluid, gave recovery in one fusion of 96 to 99% and no gas losses. Basic fluxes showed some retention of osmium by the slag and noticeable gas losses.

The iron nail assay was tried with pyritic ores salted with ruthenium or osmium and in both cases proved to be entirely unsatisfactory because much of the precious metal together with some lead clung tenaciously to the nail. Except as noted for certain fluxes with osmium (basic fluxes and one acid flux) there were no appreciable losses of ruthenium or osmium as volatile products during the crucible fusion. This was true even of the niter assays of certain pyritic ore samples. Evidently the reducing conditions of the fusion do not permit the production of volatile oxides.

CUPELLATION LOSSES

The examination of cupellation losses proved to be very interesting. Ruthenium showed high losses, even on partial cupellation to a button weighing 6.5 grams but the loss was to the cupel, not to the air as volatile oxides. Presumably, then, lower oxides of ruthenium are formed and may be absorbed by litharge. When buttons containing 5 mg. of osmium and 100 mg. of silver were completely cupelled almost all the osmium was lost, mostly as vapor but a small amount to the cupel. Partial cupellation of buttons, from which silver was omitted, to a weight of 5 to 7 grams showed a significant loss as vapor and to the cupel, the loss amounting to 5 or 10%.

Cupellation losses of iridium were examined by preparing synthetic buttons with test lead and iridium sponge and subjecting these to an ordinary cupellation. The beads were parted with nitric acid and the insoluble residue determined as iridium with allowance for a cupellation blank. Even when the silver to iridium ratio was as high as 200 to 1, small losses of iridium were observed. Black particles of iridium oxide were scattered about the surface of the cupel near the silver bead. This mechanical loss of iridium is presumably due to the very low solubility of iridium in silver. A comparable study of the cupellation of buttons containing rhodium remains to be done.

CONCENTRATION BY ION EXCHANGE

A procedure of an entirely different sort for concentrating the platinum metals, or at least of separating them from moderate amounts of associated base metals, is being examined in this laboratory. This involves the use of ion exchange resins of the anion exchange type. Advantage is taken of the fact that in dilute solutions of chlorides the platinum metals occur mainly as anionic complexes like chloroplatinate ($PtCl_6^{--}$) while the base metals are present largely as cations or cationic complexes. The work has not progressed to a point where these separations can be included within a scheme of analysis.

METHODS OF DISSOLVING

The dissolving of platinum metals presents a number of special problems. The behavior of the metal toward dissolving reagents is markedly influenced by its state of subdivision and also by its purity. The most reactive forms are the blacks; sponges and powdered metal are less reactive than blacks but usually much more reactive than compact metal. No sharp line of demarcation can be drawn between these states of fineness so that a good deal of uncertainty and many apparent contradictions have found their way into the literature dealing with dissolving these elements.

One of the commonly practiced techniques for decreasing the compactness of these metals is to form an alloy by fusion with a more active metal and later to dissolve the active metal with an appropriate acid. Lead is frequently used for this purpose when preparing scrap platinum metals, sweepings, and the like for refin-

ing or for analysis. Zinc or tin are also used in the same way. Silver is always added in moderate amounts to ores or buttons preparatory to cupellation in order to render certain of the platinum metals soluble when the bead is parted by acids.

Among the compact metals, palladium is attacked by hot concentrated nitric acid and by boiling sulfuric acid. The latter acid slowly attacks platinum and rhodium. Both platinum and palladium are dissolved by aqua regia. The remaining metals are resistant to all single acids and to aqua regia. When the metals are very finely divided they are more susceptible to attack by acids. Thus, finely divided rhodium can be dissolved by hot concentrated sulfuric acid. Ruthenium, in a fine state of division is attacked by aqua regia; the osmium is attacked by fuming nitric acid. Potassium hydrogen sulfate or potassium pyrosulfate when fused will dissolve finely divided rhodium with the production of some type of sulfate.

Alkaline oxidizing fusion mixtures are effective for rendering finely divided ruthenium or osmium soluble. Sodium peroxide, or potassium hydroxide mixed with potassium nitrate or potassium perchlorate, will convert the metal to a water-soluble ruthenate or osmate during fusion. Platinum and palladium are badly corroded by these fused reagents, and all the platinum metals, if they are finely divided enough, are converted by such oxidizing fusions to forms which are water-soluble or acid-soluble. Molten alkali cyanides also will dissolve appreciable amounts of platinum, palladium, or rhodium.

Aqueous solutions of sodium hypochlorite (chlorine in alkali) rapidly dissolve finely divided ruthenium or osmium. This method of dissolving ruthenium is used routinely in this laboratory and it is very convenient.

CHLORINATION

One of the most satisfactory methods for rendering each of the platinum metals water-soluble is the direct chlorination of the metal, preferably on a bed of sodium chloride. This technique has been known for many years and has been applied recently to several problems in this laboratory (*10*).

Procedure. An examination was made of the chlorination of the pure metals alone and of the metals covered by dry sodium chloride. The apparatus consisted of a U-shaped silica tube heated by an electric furnace. A porcelain boat containing the sample was placed near the bend of the outer arm of the U. Chlorine was dried before passing through the tube by means of sulfuric acid and phosphorous pentoxide. The exit gases were bubbled through two receiving bottles usually containing 6 *N* hydrochloric acid.

Under these conditions the metals were completely converted to chlorides or chloro complexes. Of the platinum metals, only ruthenium and osmium were partially carried through the apparatus and caught in the gas-receiving bottles. Some of the metals produced a sublimate at the cooler end of the tube. Ruthenium and gold, and also lead, produced a considerable amount of this deposit, while osmium, iridium, and platinum produced slight amounts of sublimate. Rhodium and palladium produced none.

Results. The chlorination of these metals revealed some curious phenomena for which no adequate explanation seems available. In the chlorination of platinum, for instance, part of the metal was transferred several inches through the tube and condensed as a chloride on a cold surface. The temperature in the hot part of the tube was higher than the dissociation temperature of any known chloride of platinum, and yet platinum shows no appreciable vapor pressure at this temperature. Ruthenium produced two quite different products as sublimate. These differed widely in appearance and properties, but both were unmistakably ruthenium trichloride (*11*).

The residues in the porcelain boat proved to be soluble in 0.1 *N* hydrochloric acid in all those cases where sodium chloride formed part of the charge. When no sodium chloride had been used the residues did not dissolve in this acid.

By this chlorination procedure it was shown that various weights of iridium were quantitatively converted to soluble forms from which the metal could be recovered by hydrolytic precipitation. It was also found possible to convert various native alloys of the platinum metals into acid-soluble products. In the analysis or refining of native platinum part of the metal resists prolonged attack by aqua regia; this part is generally said to consist of the alloy iridosmine, iridium, and a certain amount of nonplatiniferous material. Iridosmine is found in South Africa, Tasmania, and the Urals.

These naturally occurring alloys are sometimes brought into solution only with great difficulty by alkaline fusions and acid extractions. By treatment with chlorine on a bed of sodium chloride, a Tasmanian iridosmine which had resisted complete attack by other methods was brought into solution. Granular specimens of iridosmine and of native platinum were also converted to acid-soluble products in the same way. The conversion of these refractory alloys to soluble products in the absence of sodium chloride was accomplished, but was too slow to be practicable.

SEALED-TUBE CHLORINATION

A significant advance in dissolving iridium and platinum-metal alloys which do not respond to ordinary acid treatment has been made by Wichers and his associates (*19*) at the National Bureau of Standards. In this procedure, the sample to be dissolved is heated in a sealed glass tube with a solution of concentrated hydrochloric acid containing oxidizing agents. The latter include chlorine, fuming nitric acid, sodium chlorate, or perchloric acid. Special care must be taken in the filling and sealing of these tubes. If the amount of sample and acid requires a tube larger than 20 cm. by 4 mm., the sealed tube should be heated in a steel bomb. The temperatures of heating are sometimes as high as 300° C. and pressures as great as 300 atmospheres may be expected inside the tube. Where larger tubes and a steel bomb are used, it is recommended that dry ice be added to the bomb in order to build up a compensating pressure outside the tube. It is as well to add sufficient calcium carbonate to the bomb to neutralize the acid should there be an unpremeditated breakage of the glass tube.

Wichers and coworkers have shown that this procedure will dissolve iridium, iridosmine, and a variety of platinum metal alloys. The method possesses one advantage over chlorination in that comparatively large amounts of salt are not introduced into the sample; this might be an important consideration in preparing samples for spectrographic examination or separation by ion exchange. However, chlorination is a somewhat less demanding technique.

DISSOLVING PREPARED ALLOYS

A somewhat different approach to the dissolving of platinum metals, with special attention to iridium, is proposed by Pollard (*14*). In this procedure, the sample is alloyed with tin; the latter is said to dissolve all the metals readily. The tin alloy is then dissolved by heating in a solution of lithium sulfate in concentrated sulfuric acid. Two hours' heating is sufficient to dissolve 10 mg. of iridium, while rhodium is obtained in solution in much less time. Platinum and gold are left partly precipitated by this treatment, but these can be brought back into solution with the other metals as double sulfates. The unusual statement is made that "the platinum metal sulfates are more reactive than the chloro acids which result from an aqua regia attack, and reactions are possible . . . which do not occur in chloride solutions."

Alloying the platinum-metal sample with zinc, and then dissolving out the active metal is one well-known method of dispersing the precious metal so as to render it more easily susceptible to chemical attack. Gilchrist (*12*) recommends that the fusion be done at red heat in a silica crucible with 10 parts of zinc and a

cover of zinc chloride. After at least 1 hour the crucible is cooled, the ingot removed, and treated without crushing, because of its brittleness, with dilute hydrochloric acid.

Fusion of a sample of mixed platinum metals with lead in a carbon crucible is recommended by Schoeller and Powell (*16*) in order to render palladium, platinum, and rhodium soluble in acids. The fusion produces a button containing the platinum metals which is then subjected to a parting with nitric acid. This type of procedure is used by Gilchrist for the determination of iridium alloyed with certain other platinum metals (*9*).

PARTING OF BEADS

The cupellation of buttons containing the platinum metals plus deliberate additions of silver produces beads which are ready for the traditional parting procedures. It is recommended that where a complete analysis is required for the platinum metals cupellation should be avoided and the button should be parted directly. However, in the parting assay as applied to platinum metals two possible parting acids may be used; the choice of the original parting acid will dictate certain of the subsequent stages in the separation of the metals. It has been found that when nitric acid is used for parting of a bead containing platinum and silver in certain established ratios, the platinum dissolves along with the silver and most of the palladium. The platinum seems to pass into solution in a colloidal form. Sulfuric acid, on the other hand, causes the dissolving of the silver and part of the palladium, but leaves gold and platinum unaffected.

These distributions actually depend to quite an extent on the relative proportions of the metals present, and deliberate addition of silver and gold is necessary to achieve the separations. The residue from a sulfuric acid parting may be recupeled with silver and the resulting bead parted with nitric acid to remove the platinum. The weight of platinum, then, is the difference in the weight of the insoluble residue from the two partings.

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Chemical Methods for Separating and Determining Metals Contained in Platiniferous Materials

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BEFORE World War I the National Bureau of Standards had published a few papers which dealt with physical properties of the platinum metals. In 1917 William Francis Hillebrand, chief of the bureau's Chemistry Division, initiated a program of chemical investigation of the platinum metals, the object of which was the development of methods for preparing the metals in a degree of purity adequate for the most exacting requirements, and the development of methods for analyzing platiniferous materials. To appreciate the advances that were made in the next 25 years in perfecting methods for analyzing platiniferous materials, it is well first to examine the state of the analytical chemistry of the precious metals at the beginning of World War I.

TRADITIONAL METHODS

Historical. Holtz (*20*), after considering the methods (*1, 2, 4, 5, 21*) which had been proposed for the analysis of native grain platinum and platinum alloys, schematic diagrams of which are reproduced in the book published by Duparc and Tikonowitsch (*6*), attempted to incorporate their desirable features, together with some of his own devices, into a procedure which he used to analyze native platinum. Holtz's modifications, however, added little to the solution of the riddle of analyzing crude platinum. Two of the methods just cited deserve attention—namely, that of Deville and Stas for the analysis of platinum alloys, and that of Leidié, which was later developed at the National Bureau of Standards into a procedure for analyzing dental gold alloys (*10*).

An important contribution to the analytical chemistry of the platinum metals made at the University of Geneva was the application by Wunder and Thüringer (*25*) of dimethylglyoxime to the separation and determination of palladium. The precipitation of palladium by dimethylglyoxime deserves a place in the front rank of analytical reactions. Its very excellence serves to show by contrast how great are the shortcomings of some of the traditional analytical methods for the platinum group.

Separation of Platinum, Palladium, Rhodium, and Iridium from One Another by Ammonium Chloride. The most common operation in the analysis of platiniferous material has been the precipitation of platinum as ammonium chloroplatinate. This reaction has been generally used to separate platinum from rhodium and palladium, and, in some schemes of analysis, from iridium after reducing this metal to the trivalent state.

The outstanding feature in developing reliable procedures for the analysis of platiniferous materials was the utilization of hydrolytic precipitation under conditions of controlled alkalinity. By this means palladium, rhodium, and iridium were quantitatively separated, either singly or collectively, from platinum, and osmium, ruthenium, palladium, rhodium, and iridium were individually precipitated, after isolation, for determination. The extension of the idea of applying hydrolytic precipitation made possible the separation of the platinum metals from base metals, and led to some simple separations of base metals from one another.

The convenience of this method of separation is so great that the analyst has been prone to ignore its inherent errors. One type of error results from the persistent contamination of the platinum salt by rhodium and iridium, even though these metals be trivalent, and, to a lesser extent, by palladium. The other error occurs because ammonium chloroplatinate is appreciably soluble. It is true that the solubility of the platinum salt can be reduced to an amount which may be negligible in some analytical procedures, by adding a large excess of ammonium chloride and digesting the solution. These conditions, however, greatly increase the contamination of the salt by the other platinum metals. It is not at all unusual, for example, if a small amount of rhodium is present, for the familiar orange-yellow compound to turn bright green as the digestion proceeds. The solubility of the platinum salt also deters the careful analyst from reprecipitating it one or more times to purify it. When this is done, the increase in analytical accuracy resulting from the improved separation from the related metals is offset by loss of platinum. The practical consequence is that a determination of platinum which is based on its separation from the other platinum metals by precipitation with ammonium chloride or potassium chloride can be accurate only by the accident of compensating errors.

The shortcomings of the precipitation of ammonium chloroplatinate for analytical purposes were well recognized by such early workers as Deville and Stas. In their excellent work on the analysis of the platinum-iridium alloy used to fabricate the International prototype meter, these authors discussed at length the incomplete precipitation of ammonium chloroplatinate and its contamination by other metals, especially rhodium. They showed that the degree of contamination varies with the mode of precipitation. Under the best conditions of separation, the platinum obtained in an analysis of an alloy containing 0.65% of rhodium still contained 0.2% of rhodium. Moreover, a considerable amount of platinum remained in the mother liquor and was recovered with the major part of the rhodium. They frankly regarded precipitation with ammonium chloride as a preliminary separation. A further separation was obtained by extracting the rhodium from two or three fractions, obtained by means of ammonium chloride, with molten potassium pyrosulfate. This is at best a laborious operation which must be repeated several times. Furthermore, a portion of the platinum dissolves in the pyrosulfate and not all of the rhodium can be extracted. The method offers a closer approximation to an accurate separation of rhodium from platinum than does the procedure with ammonium chloride alone and reflects credit on the efforts of its authors to determine the actual rhodium content of the material they examined. Nevertheless, it is much too tedious for routine use and not satisfactory when a high degree of accuracy is necessary.

The separation of iridium from platinum by means of ammonium chloride has the same shortcomings as the separation of rhodium from platinum. In addition, there is the difficulty of reducing all of the iridium to the trivalent state before precipitating the ammonium chloroplatinate. Too vigorous reduction of the mixed chlorides may result in a partial reduction of platinum to the bivalent condition. Frequently, the effort of the analyst has been directed toward keeping both the iridium and platinum in the quadrivalent state and precipitating the two together with ammonium chloride, in the hope of first separating them from rhodium and palladium. The subsequent separation of the iridium and platinum from each other was based on igniting the mixed salt to sponge and extracting the platinum with diluted aqua regia. Such an extraction cannot yield accurate analytical results, except by the accident of compensating errors, because iridium sponge is not wholly insoluble in aqua regia and because platinum is not completely extractable. Experience also shows that it is even more difficult to get approximately complete precipitation of ammonium chloroiridate than of ammonium chloroplatinate. Furthermore, rhodium is entrained by the iridium salt even more persistently than by the platinum salt.

Palladium appears to be more easily separated from platinum by ammonium chloride than is rhodium or iridium. Fortunately, the analyst is now in possession of the organic reagent dimethylglyoxime, and has no further worries with palladium. The only truly quantitative separation of iridium from platinum which had been developed prior to 1914 is that discovered by Deville and Stas (*5*) and used by them for the determination of iridium in alloys from which the prototype meter was fabricated. In this method the platinum-iridium alloy is melted with about ten times its weight of lead, thus producing alloys of lead and platinum which are soluble in acids, and crystalline iridium, which is virtually insoluble in aqua regia. A study of the method at the National Bureau of Standards (*9*, *17*) confirmed its accuracy and led to certain modifications which increase the ease and speed of operation. The method is an excellent one for the routine analysis of platinum alloys which contain no iron or ruthenium. In the lead fusion, ruthenium alloys itself quantitatively with the iridium, and iron nearly so. Osmium, if present, would also alloy with the iridium. However, as a method for determining iridium only, in an alloy containing iridium, platinum, rhodium, palladium, gold, and copper, for instance, it stands as a tribute to the ingenuity of its authors.

APPLICATION OF HYDROLYTIC PROCEDURES TO SEPARATION OF PLATINUM METALS

SEPARATION FROM ONE ANOTHER

Hydrolytic Precipitation. The precipitation of insoluble hydroxides of the platinum metals as a means of separation from platinum is not a newly observed phenomenon. Over a century ago milk of lime was added to solutions of native platinum in the process of refining at the Russian Mint. Claus (*3*), the discoverer of ruthenium, discussed the elimination of impurities by this method. In 1914 Mylius and Mazzucchelli (*22*) used a solution of sodium bicarbonate in bromine water for the collective precipitation of impurities in the approximate analysis of commercial platinum. Somewhat later, Wichers (*24*), modifying the method of Mylius and Mazzucchelli, developed a hydrolytic procedure for separating rhodium from platinum, and made observations on the behavior of the other platinum metals.

In a series of researches Gilchrist (*12–16*) developed a complete system of analysis for the platinum group, in which the method of hydrolytic precipitation was utilized. A discussion of this method is given in the proceedings of the Ninth International Congress of Pure and Applied Chemistry (*18*); the analytical procedure is described in the *Journal of the American Chemical Society* (*19*) and in "Applied Inorganic Analysis" (*7*).

These researches revealed that there were some ranges of hydrogen ion concentration within which the members of the platinum group, with the exception of platinum itself, are completely precipitated by hydrolysis, when in the form of their chloro acids. For osmium the range appears to be about pH 1.5 to 6, with optimum conditions at pH 4; for iridium, pH 4 to 6; whereas for rhodium and palladium an alkalinity equivalent to pH 6 is the minimum that will ensure complete precipitation. For ruthenium the conditions appear to be such that little variation from pH 6 is permissible. Palladium, rhodium, and iridium are most advantageously precipitated in the presence of sodium bromate, and in the complete analytical procedure it is recommended that the neutralization be finally carried to pH 8 to make certain that palladium and rhodium are completely precipitated. This alkalinity has no disturbing effect on the iridium precipitate.

Not all reagents which can furnish the necessary hydroxyl ion concentration are suitable as neutralizing agents, because some of them—for example, nitrites, phosphates, and ammonium hydroxide—convert the chloro compounds of the platinum metals into other types of compounds, rather than into insoluble hydroxides.

The acidity or alkalinity at which the platinum-metal hydroxides are to be precipitated cannot usually be controlled by means of an indicator added directly to the solution. Solutions of the platinum metals are highly colored, and the precipitates obscure observation of the indicator. Furthermore, some of the reagents, such as bromate, destroy the indicators. Nevertheless, it is possible to utilize indicators in a very simple manner. The operation of testing is performed by lifting the stirring rod above the level of the solution and adding a drop of the indicator to the drop which has clung to the end of the rod. The stirring rod is then replaced in the solution, with no loss of material. This method of testing is not that of the usual "outside indicator." The end point determined in this way is practically identical with that determined by adding the indicator directly to the main body of a solution.

The indicators which have proved most useful in controlling hydrolytic precipitations are the sulfonphthaleins, in the form of their monosodium salts, at a concentration of 0.01%. These indicators are: thymol blue, which changes from red to orange at about pH 1.5, in the direction from acid to alkaline, and from yellow to blue at about pH 10; bromophenol blue, yellow to blue at pH 4; bromocresol green, yellow to blue at pH 4.7; chlorophenol red, yellow to red at pH 6; bromocresol purple, yellow to blue at pH 6.3; bromothymol blue, yellow to blue at pH 7; cresol red, yellow to pink at about pH 8; and xylenol blue, yellow to blue at an alkalinity slightly greater than pH 8.

Separation of Platinum Metals from One Another. Separation of Palladium, Rhodium, and Iridium from Platinum, by Hydrolysis. The superiority of the hydrolytic method in effecting the separation of platinum from palladium, rhodium, and iridium lies in the fact that the separation is clean-cut, simple, and quantitative. If the separation is effected in the presence of bromate, the hydroxides settle well, are readily filtered, and contain so little platinum that the separation obtained by a single precipitation is superior to that obtained by many commonly used procedures, and need be repeated only once to attain strictly quantitative accuracy.

Palladium, rhodium, and iridium are readily oxidized by adding a small amount of sodium bromate to the hot, slightly acidified solution prior to neutralization. The essential purpose of the bromate is, of course, to ensure the oxidation of these metals to a valency higher than that at which they normally exist. The addition of bromate has the further advantage that it retards the reaction of the chloroplatinate radical with hydroxyl ions. The way in which it does so is as yet unexplained, but the effect is unmistakable. It is not really necessary, however, to add bromate for the purpose of retarding the hydrolysis of the chloroplatinate radical, because this radical hydrolyzes so slowly at pH 6 and at the concentrations of platinum usually handled in analytical work that there is no interference. In any case, the first stages of the hydrolysis of chloroplatinate do not result in the formation of insoluble compounds.

Isolation of Palladium. The ideal conditions for the application of dimethylglyoxime to the isolation of palladium, in the analysis of platiniferous materials, exist when the platinum has first been completely removed. The hydrolytic method of treatment removes platinum simply and efficiently. With platinum completely eliminated, the problem of isolating palladium with dimethylglyoxime is greatly simplified. With the amounts of palladium, rhodium, and iridium ordinarily handled analytically, a single precipitation of palladium by dimethylglyoxime separates this metal from rhodium and iridium without contamination.

Separation of Rhodium and Iridium from Each Other. The separation of rhodium from iridium has long been one of the most difficult of the analytical problems of the platinum group of metals. A strictly quantitative separation of these two metals from each other was accomplished by the reducing action of titanous chloride (*14*). The method was based on a qualitative procedure of Wada and Nakazono (*23*), and its successful development came about through the ability to redissolve the precipitated metallic rhodium in boiling sulfuric acid. It was found that less contamination of the rhodium by iridium occurred if the precipitations were made in a solution containing the two metals as sulfates. Since the second precipitation had to be made in sulfate solution, there was no reason why the first should not be done so too. With the quantities of rhodium and iridium handled analytically, two precipitations of the rhodium as metal suffice to effect quantitative separation.

When the operation is over, the considerable quantity of titanium which has been added is readily accomplished with cupferron, which also acts as a scavenger. The iridium is finally recovered by hydrolytic precipitation of its hydrated dioxide.

Isolation of Osmium. Distillation of the tetroxide of osmium, usually from a solution acidified with nitric acid, has been universally used to separate this element from the other platinum metals. It was found (*13*) that the form in which the osmium exists in solution has a marked effect on the speed with which it is eliminated. If it is in the form which results when an osmium-bearing material is fused with alkaline reagents, such as sodium hydroxide and sodium peroxide or nitrate, it is eliminated completely in about 1 hour from a boiling solution which contains at least 10% of its volume of free nitric acid of specific gravity 1.4. The same thing is true if the osmium exists as bromo-osmate, but if it is in the form of chloro-osmate as much as 8 hours may be required to complete the distillation. In the latter case it is better, if possible, to distill from concentrated sulfuric acid. Under these conditions osmium is quickly separated as the tetroxide. Strangely enough, on the other hand, if the osmium exists as the bromo-osmate it is eliminated very slowly from boiling concentrated sulfuric acid. The addition of a small amount of nitric acid to the sulfuric acid solution further expedites the elimination of osmium. However, nitric acid should not be added to the sulfuric acid if ruthenium is present, since ruthenium tetroxide is slowly formed under these conditions. In the absence of nitric acid ruthenium tetroxide is not formed in the boiling concentrated sulfuric acid, and the separation of osmium from ruthenium, as well as from the other metals, is complete. The separation of osmium is also complete when the osmium tetroxide is distilled

from a nitric acid solution (containing little or no sulfuric acid), if the concentration of nitric acid does not exceed about 40% by volume of the concentrated acid. A complete separation of osmium from the other platinum metals is thus found to be possible by the traditional method, if proper precautions are observed.

ISOLATION OF RUTHENIUM. The traditional method for separating ruthenium from the other platinum metals, except osmium, is to saturate an alkaline solution of the metals with chlorine, and to remove by distillation the ruthenium tetroxide thus formed. The process of adding fresh alkali, saturating with chlorine, and distilling must be repeated several times, if even an approximately complete elimination of ruthenium is to be achieved. The cause of the incomplete elimination of ruthenium in this process probably lies in the entrainment of ruthenium by the precipitates of iridium or other hydroxides which are formed when the alkaline solution of sodium hypochlorite is changed to a nearly neutral solution of sodium chlorate, by heating. The precipitate of iridium which is produced under these conditions catalytically decomposes chlorate and bromate with the production of oxygen.

To avoid the difficulty encountered in eliminating ruthenium from an alkaline solution by means of chlorine, a procedure (*15*) was developed at the National Bureau of Standards by which ruthenium tetroxide is distilled from a solution sufficiently acid to prevent the precipitation of iridium. It was found that bromic acid, produced by adding sodium bromate to a solution containing about 5 ml. of free sulfuric acid of specific gravity 1.84 in 100 ml., will oxidize ruthenium to its tetroxide and permit its complete removal by distillation. The best conditions obtain if the ruthenium has first been converted to ruthenium sulfate. If the ruthenium exists as the chloride, the distilling operation will require about 4 hours; if it is in the form of sulfate, only 2 hours are required. The presence of the other platinum metals in the solution, or even of finely divided platinum, which is formed during the conversion of chlororuthenate to ruthenium sulfate by fuming with sulfuric acid, does not interfere with the complete elimination of ruthenium tetroxide. The conversion of the ruthenium to its sulfate, prior to distillation, has the advantage of eliminating chlorides. If present, chlorides appear to cause a trace of ruthenium, probably in the form of the dioxide, to deposit on the glass surface near the top of the distilling flask. This deposit is not readily removed.

RECOVERY AND DETERMINATION OF INDIVIDUAL PLATINUM METALS. A very suitable reagent in which to absorb osmium tetroxide quantitatively, and also ruthenium tetroxide, consists of 6 *N* hydrochloric acid saturated with sulfur dioxide. This reagent reduces these tetroxides and forms chloro-osmic acid and chlororuthenic acid, respectively. From the evaporated solutions, after destruction of sulfito complexes, osmium and ruthenium are precipitated as hydrated oxides. That of osmium cannot be caught on filter paper and ignited in air, as are the precipitates of the other five platinum metals. It is best caught in a platinum filtering crucible which has a filtering pad of platinum sponge, known as a Munroe or Neubauer crucible. The precipitate is ignited in hydrogen, the hydrogen is displaced by carbon dioxide, and the metallic residue is weighed. Whenever the hydrated oxides of the platinum metals are ignited, either in hydrogen or in air, they have a tendency to deflagrate, which has been attributed to the splitting off of the water of hydration. This tendency to deflagrate is practically eliminated by impregnating the filter and precipitate with ammonium chloride or sulfate before igniting.

The hydrated oxide of ruthenium is ignited in air to anhydrous oxide, and then reduced in hydrogen to metal. The hydrated oxides of iridium and rhodium are treated similarly. However, when rhodium has been separated from iridium by titanous chloride, it is preferable to recover it as sulfide. In this instance the strong sulfuric acid solution containing the rhodium must first be treated with strong hydrochloric acid. Rhodium is precipitated easily and completely by hydrogen sulfide from such a solution, but it is only partially precipitated from its sulfuric acid solution, or not at all. The sulfide of rhodium is ignited in air to an anhydrous oxide, which is in turn reduced in hydrogen to metal.

Platinum is also recovered as sulfide, ignition of which in air yields spongy metal. Unlike rhodium, platinum retains a small but significant amount of sulfur which must be eliminated if high accuracy is desired. The elimination of sulfur is best accomplished by dissolving the spongy platinum and reprecipitating it by reduction with a reagent such as formic acid. It is necessary to adjust the acidity of the solution to a certain range in order to obtain complete precipitation. Whereas formerly it was recommended to use sodium acetate for this purpose, it is simpler and preferable merely to add sodium hydroxide until the acidity is reduced to that corresponding to the end point of bromophenol blue (pH 4): If the acidity is maintained at this concentration, reduction to metal is complete, the necessity of boiling is eliminated, and the operation can be conducted at the temperature of the steam bath. Furthermore, the reduction can be accomplished in solutions containing appreciable amounts of sodium salts, a condition which is unfavorable to the use of sodium acetate. Thus, the necessity of making a preliminary precipitation with hydrogen sulfide may often be avoided.

Palladium sulfide cannot be ignited to metal. Often the precipitate will fuse to a globule which will not decompose on strong ignition either in air or in hydrogen. Palladium, therefore, should never be determined by igniting its sulfide. It is best determined either by weighing its glyoxime compound or by igniting this compound to metal. The residue obtained is an oxide of uncertain composition which can be converted to metal by ignition in carbon dioxide. Common practice has been to reduce the oxide in hydrogen. When this is done, it is necessary to heat the metal briefly in carbon dioxide, to eliminate the absorbed hydrogen.

SEPARATION OF PLATINUM METALS FROM BASE METALS

Many of the base metals may be removed as insoluble hydroxides or hydrated oxides from a solution in which the platinum metals have been converted to soluble nitrito complexes. If a solution which contains platinum, rhodium, and iridium, in the form of their chloro compounds, is treated with sodium nitrite and heated, the chloro compounds are converted to nitrito compounds. The complex compounds formed are $Na_2[Pt(NO_2)_6]$, $Na_3[Rh(NO_2)_6]$, and $Na_3[Ir(NO_2)_6]$. Each of these three compounds is stable and is not decomposed in boiling solutions between pH 12 and 14. The palladium complex, $Na_2[Pd(NO_2)_4]$, is stable at pH 8, but it begins to decompose, probably because of hydrolysis, with the deposition of a brown precipitate, at an alkalinity approaching pH 10, and is probably all decomposed at a slightly higher alkalinity.

Many of the nonplatinic elements form insoluble hydroxides or hydrated oxides when the concentration of hydrogen ion in solution is adjusted to within the range pH 1 to 10, and particularly within the range pH 8 to 10. It is thus possible to remove collectively a considerable number of base metals (*8*, *11*).

ANALYTICAL SEPARATION OF BASE METALS FROM ONE ANOTHER BY CONTROLLED HYDROLYTIC PRECIPITATION

The advantages to be gained by controlling the alkalinity at which hydrolytic precipitations are made in analytical chemical operations do not appear to have been fully realized, nor have the possibilities for effecting separations thereby been sufficiently exploited (*11*). Experience in developing analytical procedures for the platinum metals and for dental gold alloys (*10*) has indicated that much use can be made of the precipitation of hydroxides or

hydrated oxides, if the precipitations are made under conditions of controlled alkalinity.

To illustrate the advantages of hydrolytic precipitation, consider a few familiar separations. The separation of copper from arsenic by means of polysulfide, for instance, is not sharp, and some copper sulfide tends to dissolve. Precipitation of hydrated copper oxide in a hot solution containing not more than 5 grams of sodium hydroxide in 100 ml. of solution is sometimes used to effect the separation of copper from arsenic. It is not necessary, however, to operate in a solution as strongly alkaline as this. The separation is easily accomplished if the solution is only as alkaline as pH 10. At this alkalinity a few minutes of boiling suffices to complete the precipitation and coagulation of the hydrated copper oxide and to produce a precipitate which is easily filtered and washed.

In a similar manner copper is readily separated from selenium and tellurium. Lead likewise is conveniently separated from arsenic, selenium, and tellurium if it is oxidized to the quadrivalent state. In this case the lead separates quantitatively as hydrated dioxide at pH 10. Tin likewise can be separated from copper without resort to the use of polysulfide. Chlorostannic acid hydrolyzes in acid solution and produces hydrated stannic oxide, precipitation of which is complete in the range pH 1 to 6. By operating at pH 1.5, an acidity far above that at which copper compounds hydrolyze, hydrated stannic oxide almost free from copper is produced. The small amount of adsorbed copper is completely eliminated by hydrolytically reprecipitating the tin from sulfuric acid solution at any acidity between 1 and 1.8 *N*.

Controlled hydrolytic precipitations are also advantageous when one is dealing with the elements of the ammonium sulfide group. For instance, chromium is usually separated from iron by oxidizing trivalent chromium to chromate, and precipitating the iron as hydroxide. The reaction is customarily performed in fairly strong alkaline solution with the aid of sodium peroxide. A better way to effect the separation is to oxidize the chromium in hot, slightly acid solution by means of sodium bromate, and then to precipitate the iron by neutralizing the solution to pH 10. The conversion of trivalent chromium to chromate is rapid if the solution is slightly acid. Corrosion of the glassware, which occurs in strong alkaline solution, is avoided by operating at pH 10. Cobalt, nickel, manganese, titanium, etc., as well as copper and lead, can thus be separated from chromium. In the separation of aluminum from chromium, neutralization to pH 6.5 establishes the alkalinity most favorable to the minimum solubility of aluminum hydroxide.

In certain cases reduction of the concentration of hydrogen ion causes precipitation of salts rather than of hydroxides. This situation occurs when anions of the oxy acids are present. The precipitation of these salts is influenced by the degree of acidity or alkalinity of the solution, and in many instances there exist certain ranges of hydrogen ion concentration over which particular compounds are completely insoluble—for example, lead phosphate was found to be quantitatively precipitated in the range studied, pH 4 to 10, and lead chromate was entirely insoluble in the range investigated, pH 6.3 to 8. Lead carbonate was insoluble at pH 8 when carbonate was present. Published data give approximately the following solubilities per liter of water at room temperature: lead phosphate, 0.1 mg.; lead carbonate, 1 mg.; and lead chromate, 0.1 mg. In the presence of common ions, these solubilities are undoubtedly still lower. Precipitation of such compounds finds an application in chemical separation, such as separating lead from the platinum metals in nitrite solution.

The separation of lead from elements which form oxy acids is interesting. As previously mentioned, lead is quantitatively precipitated by the chromate ion in the range pH 6.3 to 8. Under the influence of sodium bromate, lead chromate is decomposed when the alkalinity of the solution exceeds pH 7, and hydrated lead dioxide is precipitated. In a like manner, lead sulfate which is appreciably soluble, is very readily decomposed, with the complete precipitation of hydrated lead dioxide. Similar separations of lead from selenate, tellurate, and arsenate take place.

The ease with which the elements that form oxy acids are separated from other metals does not appear to be equal. Arsenic, selenium, and tellurium, in their highest states of valency, are readily separated from copper, for example, at an alkalinity of pH 8 to 10, without the addition of bromate. Vanadium, however, does not seem to be so easily separated, at least at alkalinities less than pH 10.

In the presence of bromate, arsenic is separated from palladium, rhodium, and iridium. Chromium can also be separated from these three metals, if bromate is added to the solution, but a better way is to remove the chromium as trivalent hydroxide in a solution in which the platinum metals have been converted to nitrito complexes.

An interesting possibility for separation by hydrolytic precipitation appears to be that of copper and zinc from mercury. No precipitation occurs in solutions of mercuric salts which are not too concentrated until the alkalinity greatly exceeds pH 10. Experiments showed that hydrated zinc oxide and hydrated copper oxide, precipitated at the end point of thymol blue, were not contaminated with mercury. Other separations, which depend solely on differences in alkalinity, likewise can be made, and it is probably possible to effect the separation of germanium from gallium and indium, and of gallium from indium.

Controlled hydrolytic precipitation, which has proved itself so valuable in the development of analytical procedures for materials which contain the precious metals, should be recognized as a valuable aid in effecting separations among the other elements of the periodic system.

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Reactions Involving Colored Complexes of the Platinum Metals

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Spectrophotometric measurements have been used in studying the composition of several colored products formed from solutions of the platinum metals. For the determination of reaction stoichiometry, the method of mole ratios is more widely applicable than the method of continuous variation; the latter method is not generally suitable for determining ratios higher than 4 to 1. Formation of the well-known tetrachloro complex of palladium(II) has been confirmed spectrophotometrically by the method of continuous variation. The yellow product formed by reaction of thiocyanate with osmium solution showed a 4 to 1 reaction ratio by the continuous variation method, and both 4 to 1 and 6 to 1 by the method of mole ratios. Hypochlorite reacted with rhodium(III) in a 1 to 1 mole ratio; the product was deep blue in solutions of pH near 7, yellow at high pH, and purple at low pH; the purple color could not be developed directly in acidic solution. Electromigration tests and ion exchange resins showed the blue material to be anionic and the purple substance to be cationic. The orange to red solutions resulting from the reaction of tin(II) chloride with platinum(II) contained complexes involving tin to platinum ratios of 1 to 4, 1 to 2, 1 to 1, 3 to 2, 2 to 1, 3 to 1, and 5 to 1. In the 5 to 1 reaction, oxidation of only one tin(II) to tin(IV) occurred, apparently by reduction of platinum(II) to platinum(0). On the basis of precipitation tests with strong alkali, with phenylarsonic acid, and with silver nitrate, as well as on spectrophotometric evidence, a cationic complex, $[PtSn_4Cl_4]^{++++}$, was deduced; this complex contains platinum in zero oxidation state.

THE chemical properties of the platinum elements are so strikingly similar that their separations from one another are among the more difficult of analytical procedures. Although many color reactions of the platinum metal solutions with a variety of reagents—both inorganic and organic—have been reported, the reactions applied to analytical procedures have been largely confined to microscopic examination and to spot-test methods. Many of these reactions are suited to spectrophotometric determination of the platinum elements, with the advantages that accrue in this method of measurement. The high selectivity of many organic reagents made it appear not impossible that a scheme might be devised whereby each metal in solution could be estimated by the use of a specific (or highly selective) reagent for that element, thus eliminating at least some of the tedious analytical separations involved in gravimetric methods. Furthermore, a study of the systems by methods that would give some insight into the color-forming reaction might throw additional light on the chemistry of the platinum metals. The above factors served as the impetus for initiation of a research program at The University of Texas on spectrophotometric methods for the determination of the platinum metals.

During the past four years, this laboratory has investigated the following color reactions: ruthenium with thiourea (*5*), with dithio-oxamide (*6*), and with thiocyanate (*23*); rhodium with tin(II) chloride (*20*) and with sodium hypochlorite (*7, 26*); palladium with hydrobromic acid (*3*); osmium with thiourea (*4*) and with thiocyanate (*23*); iridium with mixed perchloric, phosphoric, and nitric acids (*2*); and platinum with tin(II) chloride (*1, 17*). In each case, the optimum range for the conditions adopted and the accuracy were evaluated, and a study was made of interference by other elements, especially by the other platinum metals. In addition to the determination of single components in solution, simultaneous determination of pairs of elements by measurement of absorbancies at two wave lengths was made in the cases of iridium and palladium with mixed acids (*2*), rhodium and platinum with tin(II) chloride (*20*), and osmium and ruthenium with thiocyanate (*23*). Some work has also been done on the use of organic solvents for extraction of reaction products.

DETERMINATION OF REACTION RATIO

Several spectrophotometric methods are available for determining the reaction stoichiometry in the formation of colored products in solution. The basis of three of these methods, which have been applied in the study of the platinum metals, is outlined briefly below.

Method of Continuous Variation. This method was first proposed by Job (*13*). In the simplest case, the formation of a single product, assume the reaction

$$A + nB \longrightarrow AB_n$$

Solutions of A and B of the same molar concentration are mixed in the ratio of x liters of B to $(1 - x)$ liters of A, to give a series of solutions with varying x values. Other volume relations can be used, so long as the total number of moles of reactants is constant. A plot of absorbancy (more specifically, the difference between the absorbancy of the product and the absorbancy of unreacted component being determined) against x, the mole fraction of B, will show a maximum if AB_n is more strongly absorbing than A or B, or will show a minimum if AB_n is less strongly absorbing than A or B, at a value such that $n = x/(1 - x)$.

Vosburgh and Cooper (*22*) extended Job's method to systems in which more than one product is formed; prior to application of the continuous variation measurements, spectral curves of solutions of different integral mole ratios of reactants are determined in order to select appropriate wave lengths for subsequent measurement of the series of solutions.

The principal disadvantage of the method of continuous variation is the fact that when n is greater than 4, it cannot be determined with certainty from the plot of absorbancy against mole fraction of reactant (Figure 6).

Slope Ratio Method. Two slightly different approaches to this method have been published, one by Bent and French (*8*), the other by Harvey and Manning (*12*); the essential features of the latter method are given below. Assume the reaction

$$mA + nB \longrightarrow A_mB_n$$

in which, under a given set of conditions, only one complex is formed. If the concentration of B is constant and so large that dissociation of A_mB_n is negligible, the equilibrium concentration of A_mB_n will be proportional to the analytical concentration of A added—that is,

$$[A_mB_n] = C_A/m$$

and a plot of absorbancy against concentration of A results in a line the straight portion of which has a slope inversely proportional to m. Similarly, if the concentration of A is large and constant, the plot of absorbancy against varying concentration of B has a slope inversely proportional to n. Hence,

$$\text{Slope}_1/\text{slope}_2 = n/m$$

Mole Ratio Method. Again, consider the reaction

$$A + nB \longrightarrow AB_n$$

Yoe and coworkers (*24*, *25*) showed that if the complex is very little dissociated, a plot of absorbancy against the mole ratio of component B to component A, with the concentration of A held constant, rises steeply from the origin as a straight line for mole ratios below that corresponding to the complex formed, then breaks sharply to a constant absorbancy at the molar ratio of B/A in the complex. Alternatively, B may be held constant and A varied, the break in the curve then indicating the ratio A/B. If the complex is appreciably dissociated, the mole ratio plot shows no sharp break, but a gradual change of slope, approaching asymptotically a constant absorbancy at high mole ratios. The breaks in the curves often can be sharpened by working with solutions of high constant ionic strength.

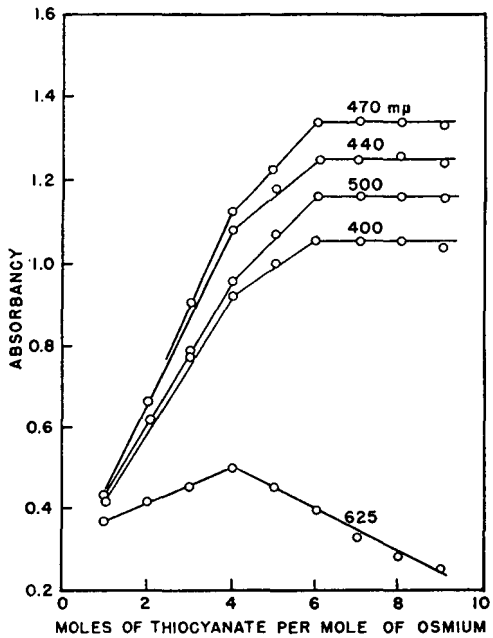


Figure 1. Osmium Thiocyanate Reaction

Previously, the mole ratio method has not been considered applicable to systems in which more than one complex is formed under a given set of conditions. Recently, Meyer (*17*) in this laboratory has given a thorough mathematical treatment of the mole ratio method for systems in which B reacts with A to form a series of consecutive complexes, and has shown that a plot of extinction coefficient against the mole ratio B/A will show a measurable change of slope if the dissociation constants for the successive complexes have the following relationship:

$$K_1/K_2 = 600\ K_2/K_3$$

By the mole ratio method, Meyer has found seven different mole ratios of reactants in the color reaction between tin(II) and platinum(II) chlorides.

PALLADIUM(II) CHLORO COMPLEX

Addition of sodium chloride solution to a solution of palladium(II) chloride caused a pronounced change in the spectral character of the solution, indicating the formation of a new species in solution. The method of continuous variation was applied by measuring the absorbancy of a series of solutions prepared by mixing x ml. (x less than 10) of 0.035 M sodium chloride with $(10 - x)$ ml. of 0.035 M palladium(II) chloride. The continuous variation curves for several wave lengths maximized at 0.67 mole fraction of sodium chloride (*20*), representing a reaction ratio of 2 to 1 for sodium chloride (chloride ion) to palladium(II) chloride, resulting in the formation of the well-known tetrachloropalladate (II), $[(PdCl_4)^{--}]$.

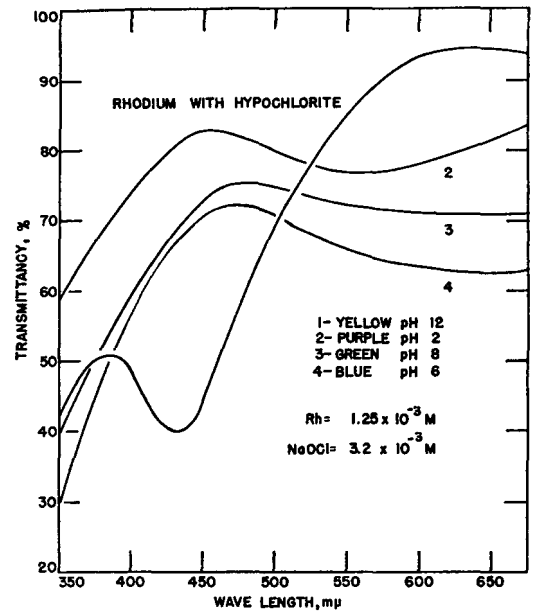


Figure 2. Spectral Curves of Rhodium–Hypochlorite Solutions of Different pH Values

The method of continuous variation does not lend itself to the determination of the reaction ratio of palladium(II) with bromide or iodide, because of the slight solubility of palladium(II) bromide and iodide unless the halide ion is present in high concentration.

OSMIUM THIOCYANATE REACTION

A method has been developed for the determination of osmium, based upon the orange color produced by addition of excess thiocyanate, in the presence of acetic acid and ethyl alcohol (*23*). Solutions in which the thiocyanate to osmium ratio varied from 1 to 1 to 6 to 1 showed colors ranging from dark brown to orange. In a plot of log absorbancy (log log $1/T_s$) against wave length, solutions containing identical kinds of absorbing materials give curves of identical shape; different concentrations of the same substance produce merely a displacement of the entire curve on the ordinate scale, but the two curves would be superimposable at all wave lengths by translation along the log absorbancy axis (*16*). Conversely, if the spectral curves for two solutions are not completely superimposable, the solutions contain different absorbing substances. The spectral curves for the 4 to 1 and 6 to 1 mole ratio solutions showed that the two solutions had nearly the same shape in the wave length region of about 400 to 525 mμ, but above about 550 mμ there was a reversal in the magnitude of the absorbancy values.

Continuous Variation Method. A series of solutions for application of this method was prepared in the usual way; acetic acid and ethyl alcohol were added, and also sodium chloride to give a final concentration of 0.2 M. After diluting to known volume, the solutions were allowed to stand for 28 hours for full color development, and the absorbancies were measured at several wave lengths. In a plot of absorbancy against mole fraction of thiocyanate, the curves for wave lengths of 400, 470, and 500 mμ maximized at a thiocyanate mole fraction of 0.8, indicating a 4 to 1 mole ratio of thiocyanate to osmium in the reaction. The data for 600 mμ gave a curve with a poorly defined maximum at about 0.67 mole fraction, indicative of a possible 2 to 1 reaction ratio.

Mole Ratio Method. A series of solutions was prepared in which the osmium concentration was held constant and the amount of thiocyanate was varied; color development was effected by the standardized procedure. The curves of Figure 1 show well-defined thiocyanate to osmium mole ratios of 4 to 1 and 6 to 1. For measurements at 625 mμ, the higher order complex shows less absorbancy than the lower complex, whereas the converse is true for measurements at the other wave lengths; these results are entirely consistent with the relative positions of the spectral curves at the various wave lengths. The fact that the absorbancy becomes essentially constant above a mole ratio of 6 to 1 indicates that higher order complexes are not formed.

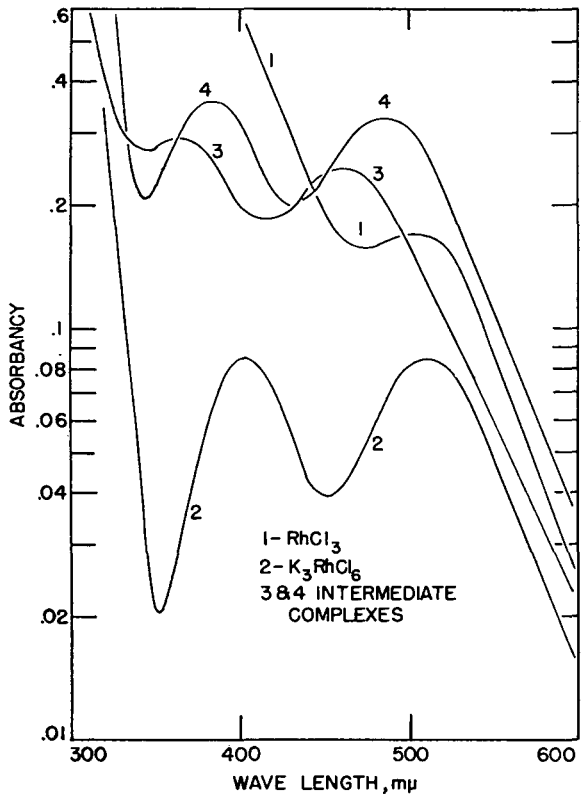


Figure 3. Spectral Curves of Solutions Containing Different Forms of Rhodium(III)

From the foregoing results, it appears that the solution contained $Os(SCN)_4$ and $[Os(SCN)_6]^{--}$ as the colored species. The colored product would not adsorb on Dowex-50 cation exchange resin, but was strongly adsorbed on IRA-400 anion exchange resin. In the method of continuous variation, for measurements at 600 mμ there was a slight indication of a 2 to 1 mole ratio which might be attributed to the formation of $[Os(SCN)_2]^{++}$.

REACTION OF RHODIUM(III) SOLUTIONS WITH HYPOCHLORITE

In the development of a method for determination of rhodium by reaction with sodium hypochlorite solution (*7*), it was found that maximum development of the blue color from appropriate amounts of rhodium (e.g., 10 p.p.m.) required a very large excess of hypochlorite and also an adjustment of the pH into the range about 5 to 7. At the higher concentrations of rhodium (e.g., about 0.001 *M*) and similar concentrations of hypochlorite used for study of the reaction stoichiometry, it was found that widely different colors were produced, depending upon the final pH of the solution: yellow-orange at pH 11 to 12, green at pH 8, blue at pH 6, and purple at pH about 2 (*26*). The spectral curves in Figure 2 show that the green color is not the result of a blue and a yellow component.

The rhodium(III) solutions used in the study of the reaction ratio were of two origins—rhodium(III) chloride obtained commercially and potassium (or sodium) hexachloro rhodate(III) $[K_3RhCl_6]$, prepared by chlorination of rhodium metal at 750° C. in the presence of excess alkali chloride. Either solution could be used equally satisfactorily for the determination of rhodium, based upon the blue color formed in the published analytical procedure (*7*).

However, in studying the reaction ratio by spectrophotometric methods, in which a correction was applied for absorbancy caused by unreacted rhodium, it was found that the spectral curves for freshly prepared solutions of the two compounds were quite different, and that the absorption characteristics of the solutions changed with age. In Figure 3, curve 1 is the spectral curve for a freshly prepared solution of rhodium(III) chloride; upon standing at room temperature for several hours or boiling the solution for a few minutes, the spectral character of the solution changed markedly approaching that represented by curve 2, which is the spectral curve for a freshly prepared solution of potassium hexachlororhodate(III). The latter solution, upon aging at room temperature for several hours or boiling for a few minutes, approached the spectral character shown by curve 1. It seems likely that these changes are associated with equilibria involving different stages of ionization and/or hydration isomerism in the rhodium salt solutions (*14*, *18*).

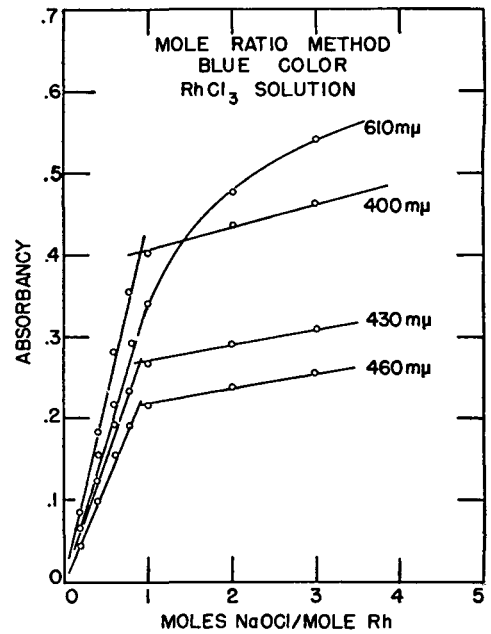


Figure 4. Rhodium(III) Chloride Reaction with Hypochlorite in Solution of pH 7

Slope Ratio Method. YELLOW SOLUTIONS. Two series of solutions were prepared: in one, the rhodium concentration was held constant and the concentration of hypochlorite was varied, and in the other, the hypochlorite concentration was constant and the rhodium was varied. All solutions were adjusted to a pH of 11, and were made 1 *M* in sodium perchlorate to give final solutions of essentially the same ionic strength. A plot of absorbancy at 435 mμ against the amount of variable component gave nearly parallel lines, indicating a 1 to 1 mole ratio in the reaction.

BLUE SOLUTIONS. The series of mixtures of rhodium and hypochlorite solutions were adjusted to pH 7 with phosphate buffer, allowed to stand for 20 minutes for full color development, and the absorbancies measured at 610 mμ. Both rhodium(III) chloride and sodium hexachlororhodate(III) were used as the source of rhodium. In the plot of absorbancy against concentration of variable component, identical slopes of the curves in each case indicated a 1 to 1 mole ratio in the reaction.

PURPLE SOLUTIONS. The purple color could not be developed directly in acid solution, but only by acidification of alkaline mixtures of rhodium and hypochlorite solutions. The final solutions were adjusted to pH 1.5 by means of hydrochloric acid–

sodium chloride buffer. Absorbancy measurements were made at 570 mμ on solutions obtained by the use of rhodium(III) chloride and sodium hexachlororhodate(III), respectively; the data were plotted as before. Although the two curves, for a given rhodium source, did not have identical slopes, the slope ratio was very nearly 1 to 1.

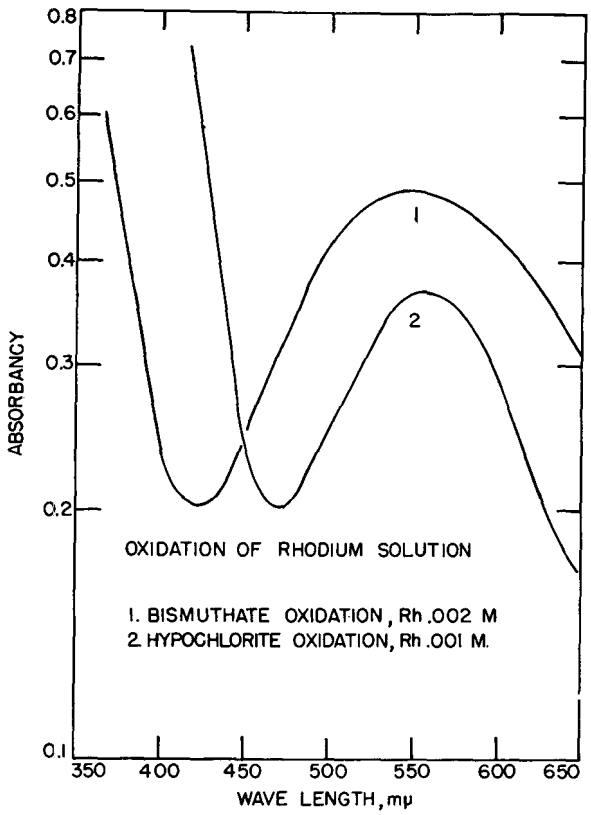


Figure 5. Comparison of Spectral Curves of Rhodium(III) Solutions Oxidized by Bismuthate and Hypochlorite

Mole Ratio Method. YELLOW SOLUTIONS. Attempts to apply the mole ratio method to the yellow solutions (high pH) were unsuccessful because of poorly reproducible absorbancies of mixtures in which the hypochlorite to rhodium ratio was less than 1 to 1. Under these conditions a colloidal system or a yellow precipitate was formed.

BLUE SOLUTIONS. Figure 4 shows the plots of absorbancy at several wave lengths against the mole ratio of hypochlorite to rhodium [as rhodium(III) chloride]; a 1 to 1 mole ratio is clearly indicated. Strangely, no break in the curve was obtained from measurements at 610 mμ, which is the wave length of maximum absorption of the blue solutions formed under the experimental conditions used. Entirely similar results were obtained by the use of sodium hexachlororhodate(III) as the rhodium source.

PURPLE SOLUTIONS. The solutions were prepared in the usual way, finally adjusting to pH 1.5. In the plots at several wave lengths, sharp breaks in the curves occurred at a 1 to 1 mole ratio of reactants.

Continuous Variation Method. YELLOW SOLUTIONS. The method of continuous variation was not applicable to the yellow solutions, for reasons given under the mole ratio method.

BLUE SOLUTIONS. In the typical continuous variation curves at different wave lengths, the maxima at 0.5 mole fraction indicated a 1 to 1 mole ratio of reactants in the color reaction.

PURPLE SOLUTIONS. A 1 to 1 mole ratio in the reaction was also shown by the continuous variation curves, which maximized at 0.5 mole fraction.

Rhodium(III)–Hypochlorite Reaction. The 1 to 1 mole ratio indicated by all of the above methods, and the known reduction of hypochlorite to chloride by gain of two electrons per mole of hypochlorite, suggests that rhodium(III) is oxidized to rhodium(V) by hypochlorite under all the conditions tested. Although rhodium in oxidation state +5 appears not to have been well characterized, it has been reported (*19*) that sodium bismuthate in sulfuric acid solution oxidized rhodium(III) to give a purple solution containing rhodium(V). A comparison of the products obtained by bismuthate reaction and by hypochlorite reaction was made by determining the spectral curves for the two purple solutions (Figure 5). Although the curves of log absorbancy against wave length have the same general shape, they are not superimposable by shift along the ordinate axis, and the intensity for a given amount of rhodium is much greater in the case of the hypochlorite reaction than for the bismuthate reaction.

In electromigration tests, the blue reaction product migrated toward the positive electrode. The product was not adsorbed by Dowex-50 cation exchange resin, but was adsorbed by IRA-400 anion exchange resin. Assuming rhodium(V) as the oxidation product, the blue reaction product might be RhO_3^- or $RhCl_6^-$. The purple reaction product migrated toward the negative electrode; it was adsorbed on Dowex-50, but not on IRA-400 resin. Cations of the type RhO^{+++} and/or RhO_2^+ may be present in the purple solutions.

Rhodium in oxidation state +4 or +6 is a good oxidizing agent (*15*); from these oxidation states, rhodium has been quantitatively determined iodometrically (*11*). It would seem plausible that if the reaction product with hypochlorite is rhodium(V), it should be an active oxidizing agent, and might be determined titrimetrically if separation from excess hypochlorite could be accomplished. The purple solution, prepared in the usual way, was passed onto a column of Dowex-50 resin; after rinsing the column to remove hypochlorite, the rhodium on the column was eluted with hydrochloric acid–sodium chloride solution; the elutriate contained 99% of the original rhodium. Excess potassium iodide was added, and the liberated iodine was titrated with sodium thiosulfate solution.

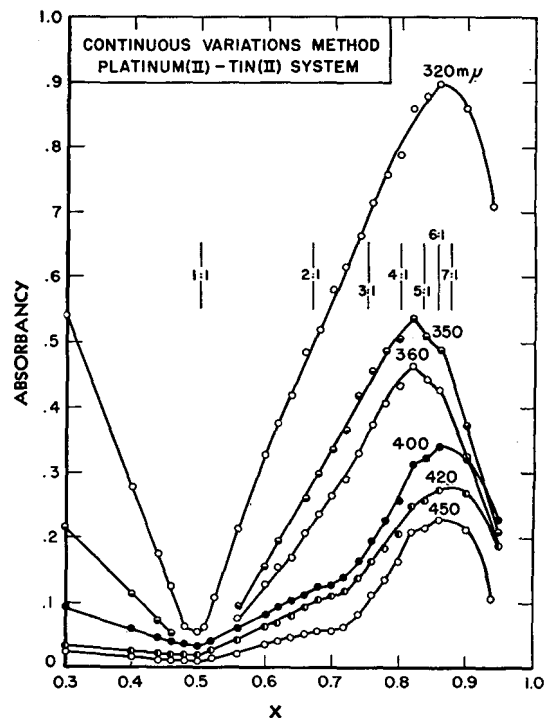


Figure 6. Reaction of Platinum Solutions with Tin(II) Chloride

X = mole fraction of tin(II)
Minimum at 0.5 corresponds to reduction of platinum(IV) to platinum(II)

When the results were calculated on the basis of electron change per mole of rhodium, it was found that the electron change varied from 1 to about 2.3 per mole of rhodium, depending upon the amount of alkali in the rhodium–hypochlorite mixture before acidification to develop the purple color. Attempts at potentiometric titrations with arsenite and with iron(II) as reductants were not successful; the titration curves did not show significant breaks. Direct potentiometric titration of rhodium(III) solution in phosphate buffer with hypochlorite solution of the same molar concentration showed a poorly defined inflection at about a 1 to 1 mole ratio of the reactants.

INTERACTION OF PLATINUM(II) AND TIN(II) CHLORIDES

The reaction of platinum(IV) with tin(II) chloride in hydrochloric acid solution is the basis for a spectrophotometric method for platinum (*1*). The red solutions are stable in the absence of oxygen, they show strict conformity to Beer's law over wide concentration ranges, readily pass through semipermeable membranes, and are well extracted by a variety of organic solvents. The properties of the system are not compatible with earlier explanations that the colored material was a protected metal colloid, or was chloroplatinous acid. The color differed from that of chloroplatinous acid, both in intensity and in the shape of the spectral curve, and identical colors were produced by the reaction of platinum(IV) and platinum(II) chlorides with tin(II) chloride. Studies designed to elucidate the reaction are described below (*17*).

Continuous Variation Method. The method was first applied using hexachloroplatinate(IV) and tin(II), each at 0.0005 *M* concentration in 1.2 *M* hydrochloric acid. Absorbancies were measured at many wave lengths between 320 and 450 mμ. In Figure 6, the minima at 0.5 mole fraction, or a 1 to 1 mole ratio, correspond to the reduction of platinum(IV) to platinum(II) as the first step in the reaction. At higher mole fractions of tin(II), maxima in the curves correspond to platinum-tin ratios of 5 to 1 or 6 to 1, and marked changes in slope of the curves for wave lengths 400 mμ and above indicate a 2 to 1 reaction ratio (mole fraction about 0.75).

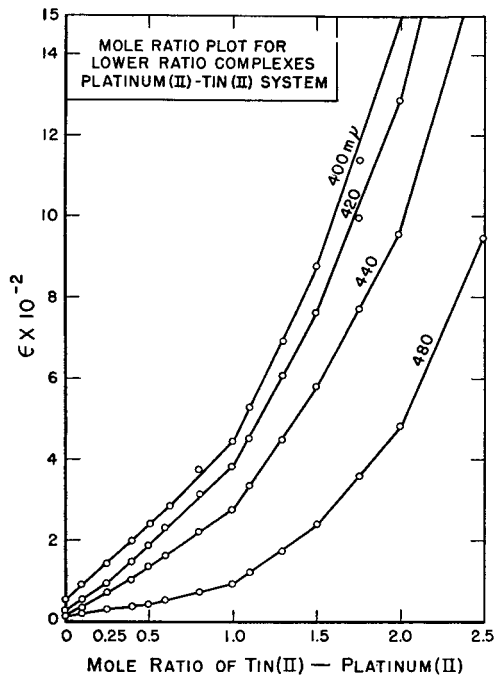


Figure 7. Platinum(II)-Tin(II) Reaction

In the continuous variation method, unambiguous deduction of reaction ratio cannot be made when the ratio is more than 4 to 1 (mole fraction 0.80); a 2% error in preparation of solutions or in estimation of the position of maximum is sufficient to produce a unit change in the mole ratio. For this reason, subsequent studies were made by the mole ratio method. Furthermore, because the first step in the reaction was shown to be the reduction of platinum(IV) to platinum(II), platinum(II) in the form of potassium tetrachloroplatinate(II) was used as the source of platinum in subsequent experiments.

Mole Ratio Method. All solutions measured were 0.010 *M* in platinum, provided by the use of weighed amounts of potassium tetrachloroplatinate(II) [K_2PtCl_4]; tin(II) chloride solution was added to give the desired concentration, and the final solution was 3.6 *M* in hydrochloric acid. All mixing, transfers, and measurements were made in nonoxidizing atmosphere. Spectral curves for solutions in which the tin to platinum ratio was varied from 1 to 10 to 5 to 1 were constructed in order to select the most appropriate wave lengths for use in making subsequent measurements.

Upon adding tin(II) chloride in definite increments to the platinum(II) solution, the original pinkish-yellow color changed to bright yellow, to orange, and finally to deep red at a mole ratio of 5 to 1 or higher. In all cases where the ratio was less than 5 to 1, the solutions showed further color development on standing. This effect was most pronounced for solutions of tin to platinum ratio of 1.5 to 1 in which a brown color developed in 20 to 30 minutes, and in one or two days the solutions were so opaque that the absorbancy could not be measured in 1-cm. cells at wave lengths shorter than about 700 mμ. Addition of excess tin(II) chloride to these brown solutions gave the clear, deep red color characteristic of the 5 to 1 solutions. With solutions of mole ratio less than 1 to 1, heating for several hours caused most of the colored material to be precipitated, apparently as metal; solutions of mole ratio greater than 2 to 1 gave no precipitate under the same conditions.

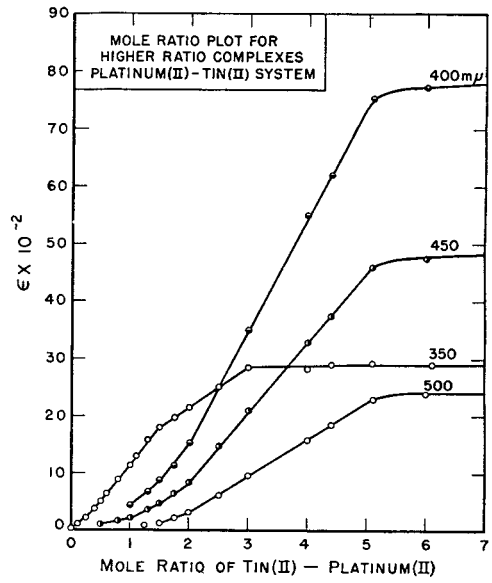


Figure 8. Platinum(II)-Tin(II) Reaction

Typical results of the spectrophotometric measurements are illustrated in Figures 7 and 8. At short wave lengths, especially below 300 mμ for the higher ratio complexes, molar extinction coefficients were of the order of 30,000 to 40,000, and the color was so intense that optical paths of 0.10 cm. (in some cases 0.005 cm.) were required to bring the absorbancy into an appropriate range for measurement. The curves of these (and other similar) figures show clearly the changes of slope corresponding to tin to platinum ratios of 1 to 4, 1 to 2, 1 to 1, 3 to 2, 2 to 1, 3 to 1, and 5 to 1.

Precipitation Methods. HYDROLYTIC PRECIPITATION. Known amounts of tin(II) chloride and potassium tetrachloroplatinate(II) in mole ratio of about 6 to 1 were treated with excess of carbonate-free sodium hydroxide and diluted to known volume. After settling the dark brown precipitate by centrifugation, an aliquot of the supernatant liquid was acidified, and the tin(II) was determined by titration with standard iodide-iodate solution; a titration control was made using the same amount of tin(II) chloride and alkali. The unprecipitated platinum was determined spectrophotometrically. From the amounts of tin and platinum taken, and the amounts of each found in the solution after precipitation, the tin to platinum ratio in the reaction was calculated to be 4.93 to 1, or approximately 5 to 1.

PRECIPITATION WITH PHENYLARSONIC ACID. Under proper conditions of acidity, phenylarsonic acid selectively precipitates tetrapositive ions. Tests showed that neither tin(II) nor platinum(II) was precipitated by this reagent from solutions 0.5 to 1.0 *M* in hydrochloric acid, and that tin(IV) was quantitatively precipitated.

Mixtures of platinum(II) and excess tin(II) were treated with excess phenylarsonic acid; a voluminous precipitate formed, containing all of the platinum. The precipitate was soluble in 4 *M* hydrochloric acid with return of the original red color. By following the same general method as used in the hydrolytic precipitation, the decrease in tin(II) concentration resulting from precipi-

tation was determined. The results, calculated as before, indicated a tin to platinum ratio of 5 to 1 in the color reaction.

A mixture of 0.60 millimole of tin(II) and 0.10 millimole of platinum(II) in solution was treated with phenylarsonic acid in 0.10-millimole increments. The first increment of phenylarsenic acid produced a dark brown precipitate, and 46% of the original platinum still remained in solution. The second 0.10-millimole quantity of phenylarsonic acid produced a similar amount of dark brown precipitate, and left only 1% of the original platinum in solution. The next two increments of phenylarsonic acid produced similar amounts of white precipitate. Further amounts of the reagent caused no visible change. Since two moles of phenylarsonic acid are required for the precipitation of one mole of a tetrapositive ion, the above results indicate that the platinum is in the form of a tetrapositive complex, and that one mole of tin(IV) is formed in the color reaction.

The above experiment was repeated, starting with 0.10 millimole of platinum(II) and 0.30, 0.10, and 0.05 millimole of tin(II) in a series of three experiments. On the basis of the 5 to 1 mole ratio previously indicated for the reaction, these quantities of reactants should leave, respectively, 0.04, 0.08, and 0.09 millimole, or 40, 80, and 90% of the original platinum unreacted. After adding phenylarsonic acid to the solutions in amounts in excess of requirements to precipitate all of the colored reaction product, the platinum remaining in the solution was found to be 38, 72, and 91%, respectively. Considering the adsorptive properties of the phenylarsonate precipitate, these findings are in good agreement with the assumption of a 5 to 1 mole ratio in the color reaction.

Determination of Chloride in the Complex. Mixtures of platinum(II) and excess tin(II) were prepared, and the chloride content of the solution determined before and again after precipitation with phenylarsonic acid, to determine the decrease in chloride resulting from the main reaction. The mole ratio of chloride to platinum in the reaction was found to be very close to 4 to 1.

A mixture of 0.10 millimole of platinum(II), 0.50 millimole of tin(II), and 0.50 millimole (an excess) of phenylarsonic acid, in sufficient hydrochloric acid to prevent precipitation, was diluted to a final acidity of 0.4 *M*, to permit precipitation. The precipitate was filtered, washed, and dried to constant weight. Based upon the platinum content of the precipitate, the calculated formula weight of the precipitate was 1727. On the basis of the precipitation tests outlined above, the precipitate should consist of $(PtSn_4Cl_4)(C_6H_5AsO_3)_2 + Sn(C_6H_5AsO_3)_2$, for which the summation of molecular weights is 1730.

DISCUSSION

The spectrophotometric methods for determining the mole ratio of reactants and the results of precipitation reactions from solutions containing an excess of tin(II) confirm the 5 to 1 ratio of tin to platinum for the principal reaction product and indicate that reaction products of higher mole ratios are not formed. The precipitation reactions require the assumption of a tetrapositive ion $(PtSn_4Cl_4)^{++++}$ or possibly its halogenated compound in solution; this complex contains platinum in zero oxidation state, formed by reduction by one tin(II) in the reaction. Similar zero oxidation states of metals have been shown to exist in tetracyanonickelate(0) (*10*) and in tetracyanopalladate(0) (*9*), and in the lower halide complexes of tantalum and niobium which have been reported to contain metallic bonds, and which are colored, stable in aqueous solutions, and very soluble in organic solvents (*21*).

In this study, little information was obtained about the lower ratio complexes; a brief study of distribution equilibrium between water and capryl alcohol indicated that a reaction product of 3 to 1 ratio of tin to platinum was the predominant species in the organic phase. It has not yet been possible to isolate any crystalline products for making x-ray studies.

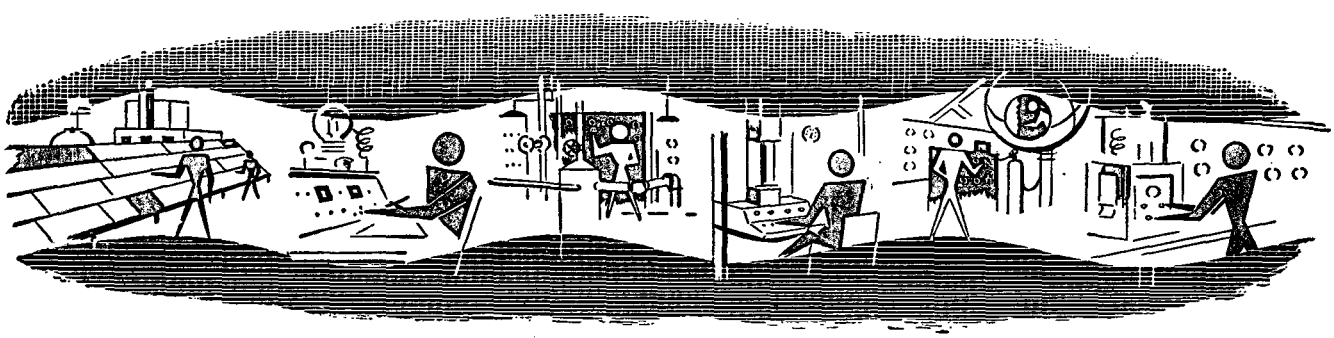
ACKNOWLEDGMENT

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Behavior of Platinum Group Metals toward Ion Exchange Resins

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The complex chlorides of palladium, platinum, rhodium, and iridium behave as anions and are quantitatively adsorbed by the anion exchange resins Amberlite IR-4B, Dowex 1, and Dowex 2, but not at all by the cation resin Amberlite IR-100. The ammine complex of palladium behaves as a cation and is quantitatively adsorbed by Amberlite IR-100 but not by anion resins. Use of this idea has led to quantitative separation of palladium from iridium, from platinum, and from rhodium, singly and in mixtures. Complete separation of rhodium and platinum from iridium, but only 95% separation of rhodium and platinum, has been accomplished. These methods are adaptable to the established Gilchrist-Wichers methods for the separation and determination of the platinum group metals.

SEPARATION of the platinum group metals (platinum, palladium, iridium, rhodium, osmium, and ruthenium) is important in analysis, in industrial production of these metals, and in radiochemical separations. Outstanding among analytical methods of separation are those of Gilchrist and Wichers (*7*) of the National Bureau of Standards, and of Schoeller and Powell (*19*). These reliable methods are admittedly laborious, and anyone who has worked with them will have wished for a simpler scheme. This is no criticism of these authors, but rather an emphasizing of the fact that the chemical separation of the platinum group metals is a complicated and difficult task (*9*).

Following the unique success achieved by the use of ion exchange in separations of the rare earths (*8, 12, 14, 22, 23*), of sodium and potassium (*3*), of amino acids (*2*), and of sodium and potassium from alkaline earth metals (*20*), it seemed worth while to investigate the behavior of these metals toward ion exchange resins. As far as could be determined, the only use of ion exchange resins with the platinum group reported in the literature was in the recovery of the metals from wastes (*16*). The loaded resins were then incinerated and the metals recovered from the ash.

The preparation, structure, and general behavior of ion exchange resins are described in several reference books (*13, 15, 17, 24*). Both cation and anion exchangers were investigated in the work reported here.

Preliminary work indicated that some resins were more effective than others. Some showed a strong affinity for the metals, as indicated by complete adsorption by a relatively small amount of resin. With others, adsorption was slight. Cation exchangers found useful are Amberlite IR-100 (Rohm & Haas) and Dowex 50 (The Dow Chemical Co.). These contain the sulfonic acid group, $-SO_3H$. Anion exchangers used were Amberlite IR-4B, Dowex 1, and Dowex 2.

The fact that both cation and anion exchangers are available makes it possible to take advantage of the cationic and anionic complexes of the platinum metals. Each of the metals platinum, palladium, iridium, and rhodium forms (*4*) a complex anion of the general type $MeCl_6^{--}$ Palladium and platinum also form cationic ammines (*5*) of the type $Pd(NH_3)_4^{++}$ There is indication that rhodium and iridium form similar ammine complexes but to a much less extent. Thus it was thought that the graded stabilities of chloride and ammine complexes (although not exactly known) might form the basis of separations.

Although the platinum group metals form many complex salts, it was the intention to work with the simpler forms first. The chlorides of the platinum metals appeared to be the simplest. Palladium, platinum, and iridium form complex chloride anions when placed in solution with excess chloride. Rhodium behaves peculiarly. Rhodium chloride made by ignition in chlorine is insoluble in water. Solutions of rhodium chloride that have been evaporated to dryness at 100° C. dissolve to give a violet-colored solution from which chloride ions cannot be precipitated with silver. Upon standing or warming, the solution becomes orange and chloride can be precipitated A change from anion to cation character is indicated by these changes.

The complex ammines of palladium, platinum, rhodium, and iridium behave as cations. Palladous ammine ion is the most stable; iridium ammine, if formed at all, is least so. These ammines are formed when ammonium hydroxide is added to a solution of the chlorides. A competition exists between the chloride and the ammonia for the platinum metal and this forms the basis of possible separations. The stabilities of both series of complexes are unknown and their relative behavior cannot be predicted.

Solutions of platinum, palladium, iridium, and rhodium were prepared from chlorides obtained from the American Platinum Works. The solutions were evaporated with nitric acid, followed by repeated evaporations with hydrochloric acid. The residues were finally heated at 100° C. to drive off excess hydrogen chloride. This method gave solutions of platinum, palladium, iridium, and rhodium of reproducible behavior.

QUALITATIVE METHODS

The following qualitative methods were found useful for detecting platinum, palladium, iridium, and rhodium when each was present alone.

Platinum. Evaporate the test portion to dryness, add 5 ml. of concentrated sulfuric acid, and evaporate to fumes. Add 5 ml. of a 40% solution of stannous chloride in 30% hydrochloric acid. An orange red color indicates platinum (*21*).

Palladium. Place 1 drop of acidic test solution on filter paper impregnated with nickel dimethylglyoxime, dry the paper over a hot plate, and then bathe it in dilute hydrochloric acid. The paper turns white except where palladium is present. Five-hundredths microgram of palladium is detectable (*6*).

Iridium. Evaporate the test solution to dryness, add 4 to 5 ml. of concentrated sulfuric acid and 2 ml. of concentrated nitric acid, and evaporate to fumes. A violet color indicates iridium. Although Sandell (*18*) describes this test as insensitive, Beamish and Hill (*1*) found it to be as sensitive as the highly recommended Pollard test, which uses perchloric acid and lithium sulfate and is sensitive to 0.5γ of iridium.

Rhodium. Evaporate the test solution to dryness, add 5 ml. of concentrated sulfuric acid, and evaporate to fumes. Add 5

[1] Present address, The Dow Chemical Co., Midland, Mich.

ml. of a 40% solution of stannous chloride in 30% hydrochloric acid. A brown color turning red indicates rhodium (*11*).

Solutions containing mixtures of the metals were evaporated to dryness and analyzed qualitatively by spectrographic means.

QUANTITATIVE METHODS

Amounts greater than 1 mg. in mixtures were estimated quantitatively by the Gilchrist-Wichers scheme. The solution to be analyzed was freed from organic matter and volatile salts by evaporation to dryness, ignition, treatment with hydrochloric and nitric acids, and evaporation to dryness. Residues, particularly those containing rhodium or iridium which did not dissolve in a mixture of hydrochloric and nitric acids, were heated in a sealed tube with aqua regia at 300° C. The resulting solution was evaporated several times with hydrochloric acid and finally evaporated just to dryness. The resulting residue was dissolved in a small amount of water and transferred to a porcelain crucible for the determination of palladium, rhodium, iridium, or platinum. Palladium, rhodium, and iridium were separated hydrolytically. Platinum was ignited to the metal in air. After the hydrous oxides were dissolved, palladium was precipitated with dimethylglyoxime, filtered through a porous porcelain filter crucible, dried at 110°, and weighed. Rhodium and iridium were separated hydrolytically and each was determined by ignition.

A colorimetric method for estimating small amounts of iridium was developed, based on the formation of a violet color in the nitric-sulfuric acid test. Maximum extinction occurs at 575 mμ when a slit width of 0.03 mm. is used. This solution obeys Beer's law over the range 0.03 to 0.12 mg. of iridium per milliliter.

RESIN EXCHANGE COLUMNS

The columns used in this work were similar to those of Tompkins (*25*), but the sintered-glass disk used to support the resin was replaced by the male part of a ground-glass joint, which was sealed off and the seal perforated to permit passage of the eluate. A wad of glass wool was placed between the perforated glass base and the resin.

The resin was prepared for use by allowing it to stand overnight in a 2% solution of the ion which would convert the resin to the desired form. This mixture was stirred until a slurry formed and then poured into the exchange column previously filled with distilled water. This procedure is imperative, to prevent air spaces in the resin bed which would lead to channeling and to prevent bursting of the column due to the swelling of the resin matrix.

ADSORPTION

Tetrachloropalladous, hexachloroplatinic, hexachlororhodic, and hexachloroiridic anions are quantitatively adsorbed by the anion exchange resins Amberlite IR-4B, Dowex 1, and Dowex 2, but not at all by cation resins Amberlite IR-100 and Dowex 50. Adsorption bands were visible on Dowex 1 and Dowex 2. Colors were more intense than in the original solutions, indicating a concentration of the metals. Rhodium, present as $RhCl_6^{---}$, gave an orange-red band; platinum, as $PtCl_6^{--}$, an orange band; palladium, as $PdCl_4^{--}$, a dark red band; and iridium, as $IrCl_6^{--}$, a very dark red band.

Osmium, present as perosmic acid, H_2OsO_5, was quantitatively adsorbed by the anion resin Dowex 1 and gave a narrow black band near the top of the column. This was unexpected, as the ionization constant of the acid is 8×10^{-13} and perosmate is colorless. Obviously, reduction to free osmium occurred.

Ruthenium, thought to be present as $RuCl_5^{--}$, was not quantitatively adsorbed by the anion resin Dowex 1. Some of the solution, colored like the original, went through the column. Three adsorption bands appeared, dark brown, light brown, and green. This indicates the probable presence of three and possibly four valence states. This behavior could be eliminated by boiling the solution with a small amount of nitric acid, after which the ruthenium was quantitatively adsorbed in a dark brown band at the top of the column.

Because osmium and ruthenium can be quantitatively removed from the other platinum metals by distillation (*10*) and because of the evidence that compounds of both are strongly reduced by the resin, it was decided to concentrate the present study upon the four remaining metals: platinum, palladium, iridium, and rhodium.

ELUTION

A high concentration of chloride might be expected to displace the platinum metal anions from the resin. The displacement is, however, slight with 0.1 *M* hydrochloric acid. More rapid elution of some of the metals was obtained with ammonium hydroxide. Complex ammines of the type $Me(NH_3)_x^{n+}$ were formed. Selectivity in elution was attained, apparently as a result of the gradations in stability of the chloride anions and the ammine cations.

Other bases thought to give complexes of the ammine type were also used as elutants. Of the bases tried, only aniline and piperidine showed general elution behavior considered satisfactory. With ammonia, aniline, and piperidine, palladium is eluted most strongly; platinum is next, followed by rhodium and iridium.

When ammonium chloride was added to the ammonium hydroxide, palladium and platinum were eluted more rapidly. Ammonium chloride decreased the rate of elution of iridium, while the rate for rhodium was not appreciably affected by the presence of ammonium chloride. It was observed with palladium that a mixture of ammonium chloride and ammonium hydroxide gave more rapid elution than either substance by itself. Apparently the $PdCl_4^{--}$ ion is displaced from the resin by substitution of the chloride ion and by the formation of the ammine $Pd(NH_3)_4^{++}$.

SEPARATIONS ACHIEVED

Palladium from Iridium. Palladium as $PdCl_4^{--}$ and iridium as $IrCl_6^{--}$ are both quantitatively adsorbed by Dowex 1 and Dowex 2. Elution of the Dowex 1 with ammonium hydroxide-ammonium chloride did not give a sharp separation of the two metals. With Dowex 2, palladium is quantitatively eluted in a spectrographically pure form when the eluent is not more than 0.025 *M* in both constituents. Iridium could not be quantitatively removed from these resins by either strong acid or strong ammonium hydroxide.

The separation of palladium from iridium is better with Amberlite IR-100, a cation resin. This has the advantage that both metals can be recovered. The mixture of $IrCl_6^{--}$ and $PdCl_4^{--}$ ions is treated with ammonium hydroxide, which converts the palladium to the cation ammine $Pd(NH_3)_4^{++}$ but has no appreciable effect on the $IrCl_6^{--}$ ion. When this mixture is passed through Amberlite IR-100, palladium is quantitatively retained while iridium is eluted, also quantitatively. Palladium can then be removed from the resin by elution with 1 *M* hydrochloric acid.

Palladium from Platinum. Like the previous pair, palladium and iridium, these two are not completely separable on Dowex 1. With Amberlite IR-100, complete separation is achieved. A mixture of $PtCl_6^{--}$ and $PdCl_4^{--}$ was treated with ammonium hydroxide and introduced into an Amberlite IR-100 cation resin column. Platinum was eluted quantitatively with an eluent containing 0.025 *M* ammonium hydroxide and 0.025 *M* ammonium chloride, while palladium remained quantitatively adsorbed. Again the palladium could be removed from the resin with 1.0 *M* hydrochloric acid. Apparently the platinum remains in the anion form in the presence of ammonium chloride.

Palladium from Iridium and Platinum. When the above experiments with Amberlite IR-100 were repeated with a mixture of palladium, iridium, and platinum as $Pd(NH_3)_4^{++}$, $IrCl_6^{--}$, $PtCl_6^{--}$, and $Pt(NH_3)_2^{++++}$, palladium was retained by the column while iridium and platinum were eluted quantitatively, showing that the presence of the third metal had no adverse effect.

Rhodium from Iridium. An attempt was made to separate rhodium from iridium by taking advantage of the observation that when individually adsorbed on Dowex 1 or Dowex 2,

rhodium is quantitatively eluted by ammonium chloride while iridium is not removed at all by this reagent. However, when the two metals are present as complex chlorides, rhodium is not quantitatively eluted from the resin by this eluent. The maximum elution of rhodium amounted to about 95% of that present. However, the rhodium eluted was spectrographically free from iridium and this method has been useful in separations of rhodium from iridium for radiochemical purposes.

Separation of Palladium, Platinum, Rhodium, and Iridium. Attempts were made to separate palladium, platinum, rhodium, and iridium by adsorbing the mixture of the complex chlorides on the Dowex 2 resin (anion) followed by elution with an ammonium hydroxide–ammonium chloride solution. Palladium was first quantitatively eluted and was free from rhodium, platinum, and iridium. Next came rhodium, followed by a mixture of rhodium and platinum. Iridium was quantitatively retained by the resin.

Better results were obtained with a combination of resin treatments. When a mixture of the four chlorides is treated with ammonia and passed through Amberlite IR-100, palladium is quantitatively retained and the rhodium, platinum and iridium are quantitatively eluted. If the eluate is then made acid with hydrochloric acid and passed through Dowex 2, the remaining three are quantitatively adsorbed. Elution with a mixture of ammonium chloride and ammonium hydroxide (0.025 *M* in each) gradually removes the rhodium and platinum and in this order. Iridium is quantitatively retained by the resin. So far the separation of rhodium and platinum has not been better than 95%—that is, platinum will appear in the eluate when 95% of the rhodium has been collected. However, all the platinum can be removed from the resin by prolonged elution. The results thus far indicate probable eventual success in making this a quantitative separation.

ADAPTATION TO ANALYTICAL SCHEME

One application of these results is the separation of palladium from platinum, rhodium, and iridium or from rhodium and iridium at the starting point of these separations. In the Gilchrist-Wichers scheme, palladium, rhodium, and iridium are precipitated as hydrated oxides, leaving platinum in solution. After the oxides are redissolved in acid, palladium is separated with dimethylglyoxime. The excess organic matter must then be destroyed before rhodium and iridium can be separated.

The separation of palladium from rhodium and iridium by ion exchange as described seems a valuable simplification at this point.

At the present time, allowing for limitations in the ion exchange separation, these four elements are separated in the following way. First palladium, rhodium, and iridium are separated from platinum as the hydrated oxides. Next the oxides are dissolved in acid and made slightly alkaline with ammonia. The mixture is passed through Amberlite IR-100 resin, which retains palladium, and rhodium and iridium appear in the filtrate. Palladium is eluted from the resin with 1 *M* hydrochloric acid. Because rhodium and iridium are not yet completely separable by ion exchange, a method developed several years ago in this laboratory by Tuthill was used for the electrolytic separation of rhodium from iridium. Rhodium is deposited electrolytically and weighed. Iridium is then precipitated hydrolytically or reduced to the free metal. This procedure takes about 4 hours.

SUMMARY

The chloride complexes of palladium, platinum, rhodium, and iridium behave as anions and are quantitatively adsorbed by anion exchange resins but are not adsorbed by cation resins. The ammine complex of palladium behaves as a cation and is quantitatively adsorbed by cation exchange resins but not by anion resins. Palladium has been separated from iridium, from platinum, and from rhodium singly and in a mixture by ion exchange. Rhodium and platinum have also been separated from iridium by ion exchange, but only 95% separation of rhodium and platinum has so far been achieved. An adaptation of the Gilchrist-Wichers scheme for the separation of palladium from a mixture of palladium, rhodium, and iridium is suggested. The rhodium and iridium may then be separated electrolytically.

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END OF 6TH ANNUAL SUMMER SYMPOSIUM

Determination of Total Nitrogen in Petroleum Distillates by Catalytic Hydrogenation

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Currently available procedures for determination of total nitrogen in petroleum distillates were found unsatisfactory when the nitrogen content was below 0.01% (100 p.p.m.). A high pressure catalytic hydrogenation process for determining total nitrogen in petroleum distillates in the range of 1 to 100 p.p.m. consists essentially of quantitatively reducing organic nitrogen to ammonia by high pressure hydrogenation in an autoclave with a nickel catalyst and absorbing the resulting ammonia on acidic alumina which is in admixture with the catalyst proper. The absorbed ammonia is determined by a conventional Kjeldahl distillation of the catalyst mixture. Interference due to sulfur is eliminated by proper choice of sample size. Data are presented on synthetic samples containing the types of nitrogen compounds found in petroleum as well as results on a variety of light petroleum distillates, both virgin and cracked.

RECENT publications on the Kjeldahl (*4*, *5*) and the ter Meulen (*3*) procedures for the determination of total nitrogen in petroleum distillates have demonstrated the utility of these methods for nitrogen in the range upwards of 0.01% (100 p.p.m.). However, attempts in this laboratory to use the Kjeldahl method on naphthas containing less than 0.01% nitrogen failed, largely because the amount of sample which can be digested is small, with the consequence that the ammonia blank for the reagents usually exceeded that recovered from the sample. The ter Meulen method was not tried in this laboratory, but the recent work of Holowchak, Wear, and Baldeschwieler (*3*) showed that the lower limit of detection was 100 p.p.m., with a possibility that refinement of technique would enable detection of 10 p.p.m.

An entirely different approach then seemed advisable. The procedure sought was one which would enable detection of nitrogen in the range of 1 to 100 p.p.m. present in petroleum distillate fractions. The low nitrogen concentration dictated that the reagent blank be negligible, and that a large sample, up to 1 liter, be used to give a convenient and accurate analysis. These requirements seemed to be fulfilled by a catalytic hydrogenation technique in which the organic nitrogen is quantitatively converted to ammonia.

The first efforts along these lines were with a high pressure bench scale hydrogenation apparatus in which the naphtha was pumped, along with hydrogen, over a suitable catalyst bed. These preliminary results showed considerable promise for the use of UOP nickel-kieselguhr catalyst for the quantitative reduction of organic nitrogen to ammonia, but the technique had to be abandoned for several practical reasons—it was difficult to recover all the ammonia and the practical aspect of repeated heating and cooling of the reactor vessel, changing of catalyst, etc., made it very difficult to maintain a leak-free system. Although it was abandoned, this work led to the idea that ammonia might be recovered by using an acidic solid in admixture with the hydrogenation catalyst. The batch-type reaction run in an autoclave proved to be a successful technique for low nitrogen concentrations in petroleum distillates.

APPARATUS

High-pressure autoclave, 3600-ml. capacity. An Ipatieff-type rotating autoclave was used in this laboratory.
Glass bomb liner with cap.
Kjeldahl flask, 800-ml.
Kjeldahl distillation apparatus.

REAGENTS

UOP nickel-kieselguhr hydrogenation catalyst. This material is available in small quantities from the Universal Oil Products Co., Des Plaines, Ill.

Pure alumina cylindrical pills. The blank on 100 grams of pills must show less than 2 p.p.m. of nitrogen. If the available commercial product is not suitable, the ammonia content may be decreased by heating at 1200° F. for about 16 hours. Heated Harshaw alumina pills were found satisfactory.

tert-Butyl chloride.
Sodium hydroxide, 50% aqueous solution.
Boric acid solution, saturated.
Standard sulfuric acid, 0.1 *N*.
Methyl purple indicator, aqueous solution, approximately 0.1%.

PROCEDURE

The sample size for catalytic hydrogenation is governed by the concentration of the total nitrogen and total sulfur in the sample being analyzed. Tables I and II can be used as a guide in choice of sample size; sulfur is usually the limiting factor and therefore Table I is generally used. If the nitrogen content is high as determined by a preliminary analysis, Table II is used. For distillates which have both high sulfur and high nitrogen contents, judicious use of both tables is necessary. The sample sizes listed are conservative estimates in order to ensure quantitative determination and are not intended as inflexible limitations.

Table I. Sample Size for Distillates Containing Sulfur

Total Sulfur, %	Sample, Ml.
0.01–0.1	1000
0.1–0.5	500
0.5–2.0	250
>2.0	200

Table II. Sample Size for Sulfur-Free Distillates

(0.01% sulfur or less)

Total Nitrogen, P.P.M.	Sample, Ml.
0–20	1000
20–50	500
>50	250

Introduce into a bomb liner 100 grams of alumina pills, 50 grams of UOP nickel-kieselguhr pills, the appropriate volume of sample, and 1 ml. of *tert*-butyl chloride. Place the charged bomb liner in an Ipatieff-type rotating autoclave and charge with hydrogen to a pressure of 750 pounds per square inch gage. Heat the bomb to 450° C. Continue heating at this temperature for 4 hours.

After the run is completed, cool the bomb to room temperature and depressurize to atmospheric pressure. Remove the bomb liner and separate the solids from the liquid product by filtration. Place the solids in an 800-ml. Kjeldahl flask. Rinse the bomb liner with at least two 50-ml. portions of distilled water and transfer quantitatively to the Kjeldahl flask. Add 300 ml. of

distilled water to the Kjeldahl flask to bring the total volume to 400 ml. Cool the contents of the flask in an ice bath.

Place a 500-ml. Erlenmeyer flask containing 25 ml. of boric acid solution and 5 drops of methyl purple indicator under the condenser, so that the tip is well beneath the surface of the liquid. Slowly pour 80 ml. of cooled sodium hydroxide solution down the inclined neck of the Kjeldahl flask. Connect the flask to the distillation condenser. Heat the distillation flask so that rapid boiling is established and maintained. When the volume of liquid in the receiving flask reaches approximately 250 ml., lower the receiver to expose the condenser tip and rinse it off with distilled water. After about 1 minute of additional distillation, turn off the heat and allow the condenser tube to drain.

The distillate may contain a hydrocarbon layer formed by hydrocarbon adsorbed on the catalyst. To facilitate the titration, carefully decant the bulk of the hydrocarbon layer, avoiding loss of aqueous solution. Titrate the distillate with standard sulfuric acid until the green color fades into gray and just beyond to the point that the gray assumes the first faint tinge of purplish pink.

Make a blank determination of the catalyst-alumina mixture following the same distillation procedure and using the same amounts of reagents as in the analysis. The ammonia should be less than 2 p.p.m. based on the total catalyst-alumina mixture. An ammonia content of alumina pills greater than 2 p.p.m. can be decreased by heating the pills overnight in a muffle furnace at 1200° F.

For very accurate work the amount of nitrogen in the form of basic nitrogen in the hydrogenated liquid product must be accounted for. The procedure used was titration with perchloric acid in anhydrous medium (*2*, *6*). Ordinarily the amount of nitrogen found in the liquid hydrocarbon after hydrogenation is less than 1% of the total and this operation is usually unnecessary.

PRECAUTIONS

Safety limits for pressure of the autoclave must not be exceeded during the determination. Generally, pressures attained in the course of the hydrogenation do not exceed 200 atmospheres at 450° C., although in one analysis in this laboratory on a sample of cyclohexane the pressure went higher and the temperature had to be lowered.

Hydrocarbon is adsorbed on the catalyst and is distilled during the distillation procedure. Care must be taken to keep the distillation receiver away from flame.

CALCULATIONS

$$\text{Nitrogen, p.p.m.} = \frac{(A - B)(N)(14{,}000)}{(V)(G)}$$

where A = volume of standard acid required to titrate distillate milliliters
B = volume of standard acid required to titrate blank, milliliters
N = normality of standard acid
V = volume of sample, milliliters
G = specific gravity of sample

RESULTS AND DISCUSSION

The basis of the method of analysis is the quantitative reduction of the organic nitrogen to ammonia by high pressure hydrogenation with a nickel catalyst. The resulting ammonia is absorbed on alumina pills which are in admixture with the catalyst proper. In order to obtain effective absorption an acidic alumina was needed, which was achieved by inclusion of a small amount of *tert*-butyl chloride with the hydrocarbon sample prior to the hydrogenation reaction. The organic halide dehydrohalogenates during the heating period to split out hydrogen chloride, which then reacts with the alumina. The resulting material is effective in quantitative absorption of the ammonia on the catalyst-alumina mixture. Following the hydrogenation step, the mixture is separated from the hydrocarbon sample and the ammonia is determined by a conventional Kjeldahl distillation.

As a test of the ability of the acidic alumina to hold the ammonia quantitatively, analyses were made of both the effluent reactor gases and the recovered hydrogenated liquid hydrocarbon; these were in addition to the determination of ammonia held on the catalyst mixture. Ammonia was determined in the gases by the method of Donn and Levin (*1*) and basic nitrogen was determined in the liquids by titration with perchloric acid in glacial acetic acid (*2*, *6*). These analyses were made on a large number of samples; in all cases no ammonia was found in the gases. Basic nitrogen in the hydrogenated liquid hydrocarbon amounted to 1% or less of the total nitrogen in most cases, although a few runs on high-sulfur stocks showed 2 to 5%. The analytical method can therefore safely disregard ammonia in the reactor gas, and basic nitrogen in the recovered hydrogenated liquid hydrocarbon can be easily titrated, if maximum accuracy is desired. All the results reported here include this nitrogen as well as that recovered from the acidic solid.

In the preparation of synthetic samples three organic nitrogen compounds were used as representative of the kind of materials that might be expected to occur naturally in petroleum distillates: pyridine, 2-methylpyrrole, and *N*-ethylcarbazole (*7*, *8*). It was anticipated that *N*-ethylcarbazole would be a severe test of the proposed method in view of the fused ring structure, and accordingly this material was used in most of the work on synthetic samples. Subsequent results on partly sulfur-deactivated catalyst showed the refractory nature of the carbazole.

Results on synthetic naphtha samples of low sulfur content are presented in Table III, where a series ranging from 4.5 to 543 p.p.m. of nitrogen was used. The data show that hydrogenation of these nitrogen compounds to form ammonia and its adsorption on the catalyst-alumina mixture can be considered as quantitative for this analytical method. Comparison of values for nitrogen found versus nitrogen added shows that the procedure is accurate, considering the low concentrations of nitrogen.

Table III. Analysis of Synthetic Hydrocarbon Samples of Low Sulfur Content

(Iso-octane solvent)

Nitrogen Compound	Volume for Analysis, Ml.	N Added, P.P.M.	N Found, P.P.M.	Error, P.P.M. N
Pyridine	1000	543	529	−14
2-Methylpyrrole	250	39.3	37.0	−2.3
	1000	22.4	18.9	−3.5
N-Ethylcarbazole	1000	154	133	−21
	700	154	141	−13
	1000	98.2	97.3	−0.9
	1000	48.6	47.9	−0.7
	1000	19.2	20.0	+0.8
	1000	15.4	18.1	+2.7
	1000	4.5	5.2	+0.7

Because sulfur occurs naturally and is known to poison nickel hydrogenation catalyst, the effect of organic sulfur compounds was investigated as summarized in Table IV. Thiophene and *tert*-hexyl mercaptan were used in order roughly to simulate naturally occurring sulfur. Sulfur is shown to have a definite effect in decreasing ammonia formation, but this can be negated by appropriate choice of sample size, since the mass of sulfur in proportion to nickel can be varied and the sulfur poisoning eliminated. The synthetic samples used here were purposely made up as high-sulfur samples, 0.5 to 1.9% sulfur, to give a severe test. In use of the method on petroleum distillates the sulfur content will very seldom be as high as this. The tables giving choice of sample size in accordance with sulfur and nitrogen contents are included to ensure freedom from the sulfur poisoning effect.

The procedure should work in the presence of olefins where depletion of hydrogen by saturation of the double bond might cause difficulty. The latter item was felt to be insignificant in view of the high hydrogen pressure, 750 pounds per square inch gage,

Table IV. Effect of Organic Sulfur and Olefins

Solvent	Charge Stock Composition N (Added as *N*-Ethylcarbazole), P.P.M.	Total S[a], Wt. %	RSH S[a], Wt. %	Hydrocarbon Solution Used, Ml.	N Found, P.P.M.	Error, P.P.M. N
Iso-octane	19.5	Nil	Nil	1000	17.0	−2.5
	21.6	0.89	0.28	900	6.9	−14.7
	22.4 (as 2-methylpyrrole)	0.93	0.35	1000	18.9	−3.5
Iso-octane–diisobutylene, 1:1	99.1	1.86	0.69	1000	6.8	−92.3
	99.1	1.86	0.69	250	99.8	+0.7
	29.2	0.52	0.15	1000	25.4	−3.8
Iso-octane–diisobutylene, 7:1	26.2	0.48	0.18	1000	22.2	−4.0

[a] Sulfur added as thiophene and *tert*-hexyl mercaptan.

but was nevertheless investigated. The results are summarized in Table IV, where it is shown that the method works nicely even in the synthetic naphtha containing a high concentration of olefin.

The data of Table IV (lines 2 and 3) show that *N*-ethylcarbazole is refractory in comparison to 2-methylpyrrole—that is, with the partially sulfur-poisoned catalyst the latter was reduced, while the *N*-ethylcarbazole gave poor ammonia recovery. Comparison of lines 1 and 2 shows the sulfur poisoning effect, while lines 4 and 5 demonstrate that by proper choice of sample size the effect of sulfur poisoning is eliminated.

The method was applied to a high-sulfur cracked naphtha, a Santa Maria coker distillate containing 2.35% sulfur, in further study of sulfur interference. The analyses as given in Table V show that the excellent precision is obtained when the size of sample taken for analysis is regulated to allow for the sulfur poisoning effect. A synthetic sample having properties similar to the coker distillate was prepared to check the accuracy of the analysis. The results show that accuracy as well as precision is excellent.

Table V. Analysis of Santa Maria Coker Distillate

Sample	Volume, Ml.	N Found, P.P.M.	Remarks
S.M. coker distillate	1000	111	Sample too large
	500	120	
	250	130	Correct amount of sample
	250	128	
	150	130	
Simulated S.M. coker distillate	250	131 (added 139)	

Properties of Samples

S.M. coker distillate	
API gr. at 60° F.	52.3
Boiling range	158° to 398° FEP
Hydrogen sulfide, wt. %	0.006
Mercaptan sulfur, wt. %	0.082
Total sulfur, wt. %	2.35
Bromine No.	67
Basic nitrogen, p.p.m.	62
Simulated S.M. coker distillate	
Solvent, 1:1 mixture of iso-octane and diisobutylene	
Sulfur	
S as thiophene, %	1.94
S as *tert*-hexyl mercaptan, %	0.067
Nitrogen, p.p.m.	
As *N*-ethylcarbazole	40
Pyridine	60
2-methylpyrrole	39
Total	139

Table VI. Analysis of Petroleum Distillates

Type of Stock	Total N, P.P.M.	Basic N, P.P.M.	Sulfur, Total, %
Virgin gasolines and naphthas			
Source			
Calif. naph., 288–360° F.	7.3	3.7	0.16
Calif. naph., 168–230° F.	5.9	1.2	0.02
Penn. S.R. gasoline	15.0	3.2	0.04
Wyo. med. naph.	4.6	1.8	0.07
Mich. S.R. gasoline	5.0	2.0	0.12
Middle East naph. (Kuwait)	3.1	<1	0.07
Penn. S.R. naph.	3.5	<1	0.03
Penn. S.R. gaso.	2.0	<1	0.03
Venezuela hvy. naph.	<1	<1	0.06
Middle East hvy. naph.	<1	<1	0.07
Mich. S.R. naph.	5.4	1.4	0.10
Penn. S.R. gaso.	5	<1	0.05
Wyo. med. naph.	2.8	<1	0.11
Cracked gasolines and naphthas			
Mid-Cont. med. naph.	4.1	<1	0.08
Visbreaker naph. Wyo. W. Tex.	30	19	0.57
	32	19	0.35
Calif. cracked naph.	184	171	1.52
Santa Maria coker distillate	130	62	2.35
Calif. therm. cracked naph	234	224	1.28
No. 2 fuel oil components			
Calif. therm. side cut	56	22	1.85
Wyo. cat side cut	210	61	1.08
Mid. Cont. therm. side cut	224	161	0.53
Miscellaneous			
Tech. methylcyclopentane	3.4	<1	<0.01
Tech. cyclohexane	1.0	<1	<0.01
C.P. benzene	1.0	<1	<0.01
Crude coal tar benzene	134	14	0.53
Tech. *n*-heptane	0.8	<1	<0.01

A large number of petroleum distillates have been analyzed, including virgin gasolines and naphthas, cracked gasolines and naphthas, and No. 2 burner oils. Some typical results are given in Table VI. The virgin gasolines showed a considerable range of nitrogen contents, from less than 1 to 15.0 p.p.m. The ratio of basic nitrogen to total nitrogen varied considerably in the cracked materials where basic nitrogen almost equaled total nitrogen in some cases, whereas in others it was only one half of the total nitrogen. In virgin naphthas basic nitrogen was as little as one fifth of the total nitrogens. (The basic nitrogen referred to is naturally occurring and is not a result of the hydrogenation.)

Variations in the mechanics of running this analysis are possible—for example, smaller hydrogenation bombs can be used along with corresponding reduction in sample size, catalyst, alumina, and normality of the titrating acid. The limit of detection may be lowered below a few parts per million nitrogen as studied. The problem would be to obtain reagents containing far less ammonia; it would not involve measurement of small amounts of ammonia produced, as there are available procedures for this purpose.

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Tetraphenylphosphonium and Tetraphenylstibonium Chlorides as Analytical Reagents

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The extensive use of tetraphenylarsonium chloride as an analytical reagent prompted this investigation of the corresponding phosphonium and stibonium compounds, which behave in a similar manner. They form insoluble crystalline salts with permanganate, perrhenate, pertechnetate, perchlorate, periodate, fluoborate, and certain complex metal chlorides such as those of mercury, tin(IV), cadmium, thallium(III), and tellurium(IV). Some of these can be weighed directly; the others can be determined titrimetrically by adding an excess of the reagent and titrating the excess with iodine to form a periodide. These salts are all extractable from aqueous solution by chloroform. The peculiar properties of these salts make them valuable analytical reagents—for example, tetraphosphonium permanganate is completely insoluble and completely extractable.

THE use of tetraphenylarsonium chloride as an analytical reagent was applied by Willard and Smith (*9*) to the determination of rhenium, mercury, cadmium, zinc, and tin. Its use for the determination of thallium was described by Smith (*5*), for platinum by Bode (*2*), for tellurium by Bode (*3*), for cobalt by Potratz and Rosen (*4*) and Affsprung, Barney, and Potratz (*1*), for technetium by Tribalat and Beydon (*7*), and for the separation of rhenium from molybdenum by Tribalat (*6*). Because it appeared probable that the corresponding derivatives of phosphorus and antimony would also be useful reagents, these compounds were prepared and their analytical properties investigated. Potratz and Rosen (*4*) investigated qualitatively the use of a number of onium compounds for the detection of bismuth and cobalt.

The preparation of tetraphenylphosphonium and tetraphenylstibonium chlorides was described by Willard, Perkins, and Blicke (*8*). The former can be prepared more easily and at a lower cost than tetraphenylarsonium chloride. In general, the ions precipitated by the phosphonium and stibonium salts are much the same as with the arsonium. Tetraphenylphosphonium chloride is more soluble and the corresponding stibonium compound is less soluble than the arsonium salt. The precipitates obtained in some cases follow the same order. However, the solubility of tetraphenylstibonium chloride is so low that its use as a reagent is extremely limited.

The presence of considerable sodium chloride is essential for complete precipitation in nearly all cases. The procedures using tetraphenylphosphonium chloride are so similar to those already described (*9*) for tetraphenylarsonium that in many cases only the necessary variations are listed here. The interfering ions are also similar.

In most cases the direct weighing of the precipitate is not feasible, because the wash solution must contain sodium chloride, although in a few cases the precipitate is so insoluble that it can be washed with water. Titrimetric methods are based upon the addition of a known amount of the reagent, and titration of the excess by iodine to form the triiodide. The precipitates, like those with tetraphenylarsonium, are readily soluble in chloroform, thus making extractions very convenient, especially for spectrophotometric methods.

TITRATION WITH IODINE

The potentiometric titration curve is similar to that found by Willard and Smith (*9*), and the precipitate is the triiodide, $(C_6H_5)_4PI_3$. The best concentration of sodium chloride is 4.0 *M*, and if more than 50 mg. of the phosphonium chloride are present it is best to add the sodium chloride after about half the iodine solution has been added. At the end point the temperature should not be over 30° C. Moderate amounts of hydrochloric acid were without effect.

A visual end point is possible, using starch as indicator and chloroform to dissolve the triiodide, but in this case sodium chloride should not be added. The precision is less than for the potentiometric method.

Oxidizing agents, such as nitric acid, give low results, as do large amounts of organic acids. Nitrate in a neutral solution does not interfere. The interfering ions are the same as in the titration of tetraphenylarsonium chloride.

The average error for 2 to 100 mg. of tetraphenylphosphonium chloride is ±0.07 mg.

DETERMINATION OF MERCURY

Analytical reagent mercury was dissolved in nitric acid, the excess neutralized with sodium hydroxide, and the solution diluted to 1 liter. One milliliter contained 5.00 mg. of mercury.

The solution of tetraphenylphosphonium chloride was standardized by titration with an iodine solution, which was standardized against arsenious oxide.

Direct titration of mercury with tetraphenylphosphonium chloride was impossible because of a lack of any suitable method of determining the end point. An amperometric method might be possible for small amounts. A gravimetric determination by weighing the precipitate of $[(C_6H_5)_4P]_2HgCl_4$ was impossible because no suitable wash solution could be found to remove the sodium chloride.

The titration of excess of the reagent, however, gave good results.

The volume of the mercuric solution was adjusted to about 100 ml. after the reagent had been added. A 2.0 to 3.0 *M* concentration of sodium chloride was most suitable. An excess of about 10 to 20 ml. of 0.01 *M* tetraphenylphosphonium chloride was added to the warm solution and the solution allowed to stand with occasional stirring for 5 minutes to 2 hours, the longer time being required for amounts of 1 mg. The solution must cool to room temperature before it is filtered through a filtering crucible and

Table I. Determination of Mercury

10-ml. excess of 0.01 *M* $(C_6H_5)_4PCl$

NaCl Concn., *M*	Total Volume, Ml.	Hg Present, Mg.	Hg Found, Mg.	Error, Mg.
3.0	40	0.50	0.5	0
3.0	60	5.00	4.98	−0.02
3.0	100	15.00	15.02	+0.02
2.0	100	50.02	50.07	+0.05
1.5	150	100.04	100.08	+0.04
1.5	200	150.06	150.8	+0.7

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washed with saturated sodium chloride solution. Free acid can be present up to 1.0 *M*, except that free nitric acid must be neutralized.

Table I shows the results obtained. Interfering ions have been mentioned (*9*).

DETERMINATION OF TIN

Stannic tin is precipitated by tetraphenylphosphonium chloride as the chlorostannate, $[(C_6H_5)_4P]_2SnCl_6$. Only a titrimetric method is possible.

A standard tin solution was prepared by dissolving reagent grade tin in concentrated hydrochloric acid through which chlorine gas was bubbled. One milliliter of the solution contained 3.96 mg. of tin and about 0.1 ml. of concentrated hydrochloric acid.

Table II. Determination of Tin

100-ml. total volume
10-ml. excess of 0.01 *M* $(C_6H_5)_4PCl$
2 ml. of HCl (sp. gr. 1.18)

NaCl Concn., *M*	Tin Present, Mg.	Tin Found, Mg.	Error, Mg.
3.5	1.98	1.96	−0.02
3.0	7.92	7.85	−0.07
3.5	39.62	39.64	+0.02
3.0	99.05[a]	98.97	−0.08
2.0	148.57[a]	148.90	+0.33

[a] Final volume 150 ml.

The procedure is the same as for mercury, except that the optimum concentration of sodium chloride is 3.0 to 3.5 *M*, not much more than 10 ml. excess of reagent should be added, the hydrochloric acid concentration should be 0.1 to 1.0 *M*, and it is unnecessary to precipitate the tin in a warm solution. Table II shows the results obtained.

DETERMINATION OF CADMIUM

Cadmium is precipitated as $[(C_6H_5)_4P]_2CdCl_4$, but the precipitate is more soluble than those of mercury and tin.

The cadmium solution was prepared by dissolving pure electrolytic cadmium in nitric acid, neutralizing with sodium hydroxide, and adding a few milliliters of hydrochloric acid. One milliliter contained 4.00 mg. of cadmium.

Table III. Determination of Cadmium

100-ml. total volume
10-ml. excess of 0.012 *M* reagent
Solution neutral to methyl orange

NaCl Concn., *M*	Cd Present, Mg.	Cd Found, Mg.	Error, Mg.
4.5	0.40	0.43	+0.03
4.5	12.00	12.04	+0.03
3.5	40.01	40.04	+0.03
3.5	80.02[a]	79.95	−0.07
3.5	120.04[a]	120.12	+0.08

[a] Total volume 150 ml.

The procedure is the same as for tin, but the optimum range of concentration of sodium chloride is 3.5 to 4.5 *M*, and a 30 to 40% excess of reagent is needed. Precipitation is best made in a warm solution, but the solution must be allowed to cool before filtering. The concentration of hydrochloric acid should be no greater than 0.7 *M*. Table III shows the results.

DETERMINATION OF ZINC

The precipitate of $[(C_6H_5)_4P]_2ZnCl_4$ is too soluble to permit a satisfactory separation of zinc.

DETERMINATION OF PERRHENATE

Tetraphenylphosphonium perrhenate, like the corresponding arsonium salt, is sufficiently insoluble to permit both gravimetric and titrimetric determination of rhenium. The procedure was the same as that recommended by Willard and Smith (*9*), except that a sodium chloride concentration of 2.5 to 3.0 *M* is necessary for the gravimetric, but only 1.5 *M* for the titrimetric method.

Table IV. Determination of Rhenium

Total volume, 100 ml.
10-ml. excess of 0.012 *M* $(C_6H_5)_4PCl$

NaCl Concn., *M*	ReO_4^- Present, Mg.	ReO_4^- Found Grav., Mg.	Error, Mg.	ReO_4^- Found, Titr., Mg.	Error, Mg.
3.0[a]	0.38	0.31	−0.07	0.33	−0.05
2.5	7.63	7.56	−0.07	7.60	−0.03
2.5	15.25	15.33	+0.08	15.30	+0.05
2.5	76.27	76.17	−0.10	76.22	−0.05
2.5	129.67[b]	129.60	−0.07	129.69	+0.02

[a] Volume was 50 ml.
[b] Volume was 150 ml.

The standard perrhenate solution, prepared by dissolving recrystallized potassium perrhenate in water, contained 7.63 mg. of perrhenate, ReO_4^-, per milliliter. Hydrochloric acid up to 3.0 *M* was not harmful. The results are shown in Table IV.

DETERMINATION OF PERCHLORATE

Tetraphenylphosphonium perchlorate is so insoluble that it may be employed in both a gravimetric and a titrimetric method. As with rhenium, both methods may be carried out simultaneously by weighing the precipitate after drying at 110° C. and by titrating the filtrate and washings with iodine.

Potassium perchlorate was prepared by neutralizing analytical reagent potassium carbonate with perchloric acid and recrystallizing the salt. A standard solution was prepared by dissolving the salt in water. This solution contained 3.61 mg. of ClO_4^- per milliliter.

To the neutral or acid solution of the perchlorate, 2.0 to 3.0 *M* in sodium chloride, was added a measured amount of approximately 0.01 *M* tetraphenylphosphonium chloride, about 10 ml. in excess. The precipitate was rapidly stirred for several minutes and then allowed to stand for 2 hours or longer. It was filtered through a filtering crucible, washed several times with ice water, dried at 110° C., and weighed as tetraphenylphosphonium perchlorate, $(C_6H_5)_4PClO_4$. The excess of reagent in the filtrate and washings can be determined by the usual potentiometric titration with iodine.

The presence of sodium chloride caused the precipitate to be more crystalline and to adhere less to the walls of the beaker. Heating the solution before precipitation had a similar effect. Concentrations of hydrochloric acid up to 2 *M* had no effect. Table V shows the results obtained with pure perchlorate solutions.

The presence of chlorate interfered with both the precipitation of tetraphenylphosphonium perchlorate and the titration with iodine. The interference was effectively removed for as much as 500 mg. of chlorate by reduction of the chlorate in acid solution

Table V. Determination of Perchlorate

Total volume, 100 ml.
Excess of 10 ml. of 0.012 *M* $(C_6H_5)_4PCl$

NaCl Concn., *M*	ClO_4^- Present, Mg.	ClO_4^- Found, Grav., Mg.	Error, Mg.	ClO_4^- Found, Titr., Mg.	Error, Mg.
3.0[a]	0.54	0.59	+0.05	0.48	−0.06
2.5	10.82	10.74	−0.08	10.77	−0.05
3.0	10.82	10.83	+0.01	10.80	−0.02
2.5	54.12	54.18	+0.06	54.20	+0.08
2.0[b]	126.28	126.22	−0.06	126.27	−0.01

[a] Total volume 50 ml.
[b] Total volume 150 ml.

with sodium bisulfite. In the presence of chlorate the procedure was as follows:

To the cold, slightly acid solution, an amount of sodium bisulfite was added equal to about five times the weight of chlorate present. The solution was allowed to stand 30 minutes and gently boiled until no more sulfur dioxide could be detected; the solution was kept slightly acid throughout this period. An excess of standard tetraphenylphosphonium chloride solution was added to the rapidly stirred hot solution and after standing 2 hours the cold solution was treated as described above. The results are shown in Table VI.

Table VI. Determination of Perchlorate in Presence of Chlorate

2.5 *M* sodium chloride
Total volume 100 ml.
18.04 mg. of ClO_4 present

ClO_3, Mg.	$NaHSO_3$ Added, G.	ClO_4^- Found Grav., Mg.	Error, Mg.	ClO_4^- Found, Titr., Mg.	Error, Mg.
50	None	20.0	+2.0	19.9	+1.9
100	None	21.9	+3.9	22.3	+4.3
100	0.5	18.08	+0.04	18.09	+0.05
200	1.0	17.95	−0.09	17.98	−0.06
500	2.5	18.15	+0.11	18.12	+0.08
1000	5.0	18.37	+0.33	18.26	+0.22

Tetraphenylstibonium chloride, like the corresponding arsenic and phosphorus compounds, reacts with perchlorate ion to form the insoluble perchlorate, $(C_6H_5)_4PSbCl_4$. This reaction permits only the gravimetric determination of perchlorate, because tetraphenylstibonium chloride cannot be successfully titrated with iodine.

The gravimetric determination was successful, but because of the low solubility of the reagent in 1.5 to 2.0 *M* sodium chloride solution the very small excess that could be present made the method impractical, unless the amount of perchlorate present was known to within 1 mg.

DETERMINATION OF PERIODATE

Tetraphenylphosphonium periodate, $(C_6H_5)_4PIO_4$, is sufficiently insoluble to make possible a titrimetric but not a gravimetric determination, as the precipitate must be washed with sodium chloride solution.

The standard periodate solution was prepared by dissolving recrystallized potassium periodate, KIO_4, in water. One milliliter of this solution contained 1.20 mg. of periodate.

Excess of standard tetraphenylphosphonium chloride was added to a cold, slightly acid solution of periodate containing sufficient sodium chloride to make the final concentration 2.0 *M*. The precipitate was allowed to stand about 2 hours, filtered, and washed with saturated sodium chloride solution. The combined filtrate and washings were titrated as usual. If the solution was heated before precipitation, the results were always low. Only a drop or two of concentrated hydrochloric acid in excess may be present, and if the solution was alkaline to methyl red, the results were inaccurate. Iodate interfered with the titration in acid solution, but interference of the acid was reduced if the solution was saturated with sodium bicarbonate. The results are shown in Table VII.

Table VII. Determination of Periodate

Total volume 100 ml.
10-ml. excess of 0.12 *M* $(C_6H_5)_4PCl$

NaCl Concn., *M*	KIO_4 Present, Mg.	IO_4^- Present, Mg.	IO_4^- Found, Mg.	Error, Mg.
3.0[a]	0	0.90	0.95	+0.05
3.0[a]	0	9.02	8.96	−0.06
3.0	0	15.03	15.01	−0.02
2.0	0	90.21	90.30	+0.09
2.0	0	102.24	102.35	+0.11
2.0	25	30.07	30.01	−0.06
2.0	100	30.07	30.14	+0.07
2.0	150	30.07	30.54	+0.47

[a] Total volume 50 ml.

DETERMINATION OF PERMANGANATE

Permanganate forms very insoluble purple precipitates of $(C_6H_5)_4PMnO_4$ and $(C_6H_5)_4SbMnO_4$ with tetraphenylphosphonium chloride and tetraphenylstibonium chloride, and may be determined gravimetrically with either reagent, but titrimetrically only with the phosphonium salt. A direct titration was not successful with either.

A standard permanganate solution was prepared in the usual way, and standardized against arsenious oxide. It contained 3.58 mg. of MnO_4 per milliliter.

A definite excess of tetraphosphonium chloride was added to the hot permanganate solution containing sufficient neutral salt, preferably not a chloride, to provide a salt concentration of 0.5 to 1.0 *M*; this was necessary to cause complete precipitation, and sodium sulfate or nitrate is preferred. The solution was allowed to stand until it had reached room temperature, filtered, washed several times with water, and dried in a desiccator to constant weight, which usually required 2 or 3 days. Heating of the dry salt at 100° C. causes decomposition. The filtrate and washings were titrated potentiometrically with standard iodine. When nitrate was added it was necessary first to make the solution just alkaline to methyl red.

The results are shown in Table VIII. Sulfuric, nitric, and phosphoric acids up to 1.0 *M* had no effect. Hydrochloric acid reduces the permanganate.

Table VIII. Determination of Permanganate

Total volume 100 ml.
1.0 *M* $NaNO_3$
10-ml. excess of 0.012 *M* $(C_6H_5)_4PCl$

MnO_4^- Present, Mg.	MnO_4^- Found, Mg. (Grav.)	Error, Mg.	MnO_4^- Found, Mg. (Titr.)	Error, Mg.
0.18	0.15	−0.03	0.17	−0.01
1.79	1.82	+0.03	1.85	+0.06
7.17	7.16	−0.01	7.12	−0.05
53.76	53.82	+0.06	53.84	+0.08
71.68	71.60	−0.08	71.72	+0.04
107.52	107.64	+0.12	107.59	+0.07

For the determination of manganese in a manganous salt, the best oxidizing agent is sodium bismuthate, in a solution containing 5 to 10 grams of metaphosphoric acid to form a soluble complex with the trivalent bismuth. The excess of bismuthate was filtered off. If the amount of soluble bismuth was not over 350 mg., 1.2 *M* nitric acid solution was also satisfactory. The errors were about the same as in Table VIII.

The same procedure with tetraphenylstibonium chloride gave results in the presence of 0.1 to 0.8 *M* sodium nitrate or 0.1 to 0.5 *M* sodium sulfate similar to those in Table VIII, but the largest amount determined was 18 mg. of MnO_4^-. An excess of 10 ml. of 0.01 *M* stibonium chloride was added. The tetraphenylstibonium chloride was standardized gravimetrically by precipitation as the perchlorate in 1.5 *M* sodium chloride solution containing an excess of perchlorate.

DISCUSSION

It may be predicted that tetraphenylphosphonium chloride can also be used to precipitate platinum, tellurium, thallium, and technetium, for which the arsonium compound has already been employed. Interfering substances have been listed (*9*), but there have been some additions and modifications. The alkali metals, alkaline earths, aluminum, manganese(II), chromium (III), nickel, cobalt, zirconium, sulfate, borate, phosphate, carbonate, acetate, tartrate, and citrate are not precipitated and do not interfere. The following ions are precipitated either completely or partially: permanganate, perrhenate, periodate, perchlorate, persulfate, borofluoride, chromate, molybdate, tungstate, thiocyanate, iodide, stannic, cadmium, zinc, platinum, ferric, gold, antimony, bismuth, titanium, thallic, tellurous, and uranyl. The interference of tin was eliminated by complexation

with bitartrate, of ferric ion by phosphate and phosphoric acid, and of titanium by metaphosphoric acid. The influence of copper in the iodine titration was eliminated by the addition of citrate. Tribalat (*6*) precipitated perrhenate from alkaline solution to separate it from molybdate. The use of fluoride as a complexing agent is restricted because of the low solubility of the arsonium, phosphonium, and stibonium salts. Although the borofluoride ion, BF_4^-, is quantitatively precipitated, an attempt to use this as a method for fluoride failed because of the rapid hydrolysis of this ion.

SUMMARY

Tetraphenylphosphonium chloride precipitates quantitatively, in the presence of sodium chloride, complex chloride salts of tin, cadmium, and mercury such as $[(C_6H_5)_4P]_2SnCl_6$. These cannot be weighed as such, because sodium chloride must be used in the wash solution. The excess of reagent may be titrated potentiometrically with standard iodine to form $(C_6H_5)_4PI_3$.

Tetraphenylphosphonium permanganate, perrhenate, and perchlorate are insoluble in cold water and therefore both gravimetric and titrimetric methods are possible. For periodate the titrimetric method only can be used.

Tetraphenylstibonium chloride may be used for the gravimetric determination of permanganate and perchlorate, but in the latter case the low solubility of the reagent makes the method impractical.

The salts are soluble in chloroform.

The average error under recommended conditions is about ±0.06 mg.

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Determination of Malic, Tartaric, and Citric Acids in Fruit by Ion Exchange Chromatography

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The methods for the determination of malic, tartaric, and citric acids in fruit are very lengthy. This paper describes a procedure in which the acids are separated by ion exchange chromatography and then determined by oxidation with permanganate. All three acids can be determined in a fruit in 8 hours by the proposed method, and the error in each determination is usually about ±0.1 mg. of acid. The sample may contain a maximum of 24 mg. of any one acid. The method is applicable to fruit, fruit juices, and fruit products.

THE methods generally used for the determination of malic, tartaric, and citric acids in fruit are those described by the Association of Official Agricultural Chemists (*1*). These procedures are very time-consuming. Wieland and Feld (*5*) suggested the use of paper chromatography for the separation and determination of the fruit acids; relative errors of about ±10% are frequently incurred by this method. Isherwood (*3*) applied partition chromatography to this problem by a procedure that involves a tedious extraction and then concentration of the fruit acids. These steps alone take 48 hours and fail to extract the acids quantitatively.

RECOMMENDED PROCEDURES

Reagents. All reagents were of reagent grade.

Eluant A was 0.0800 *M* with sodium nitrate, 0.0013 *M* with sodium tetraborate, and 0.30 *M* with boric acid. Eluant B was 0.1600 *M* with sodium nitrate and had the same concentrations of sodium tetraborate and boric acid as eluant A. Both eluants were prepared by weighing the required amounts of solutes (on an analytical balance in the cases of sodium nitrate and tetraborate) and diluting in a volumetric flask. The pH was then checked with a Beckman pH meter and, if necessary, was adjusted to 6.15 by the dropwise addition of 1 *M* sodium hydroxide.

Potassium permanganate, about 0.1 *N*, was prepared and standardized by the usual method. Standard oxalic acid of exactly the same normality as the permanganate was prepared. The normality was checked by titration with the permanganate. Sulfuric acid, 9 *M*, was prepared.

Apparatus. A glass tube 3.8 sq. cm. in cross-sectional area, provided with a sintered-glass filter disk of medium porosity, was filled to a depth of 25 cm. with Dowex-1, a strong-base anion exchange resin. The flow rate through this column was controlled by a Hoffman clamp attached to a piece of rubber tubing fitted to the lower end of the filter tube. Excessively fine particles of resin had previously been removed by decantation. As the resin was received in the chloride form, it was converted to the nitrate form by passing 0.5 *M* sodium nitrate through the column until the effluent gave a negative test for chloride. Then 1 liter of eluant A was passed through the column.

A constant-temperature bath was maintained at 30° ± 1°.

Preparation of Juice. The juice was obtained by pressing or squeezing the fruit and was centrifuged and filtered through Whatman No. 41 paper. One milliliter of the juice was then titrated with 0.1 *N* sodium hydroxide to find the total concentration of fruit acid as a guide to the selection of the proper size of sample for the elution. Sufficient solid boric acid was added to the juice to give a 0.30 *M* solution. The juice was stored in a refrigerator.

Procedure for Elution. The column was prepared for use by the passage of 500 ml. of eluant A. A sample of 5 ml. or less, containing not over 24 mg. of any one acid, was pipetted into the column, and the inside wall was rinsed with a small amount of eluant A. The column was drained until the meniscus just reached the resin. Then 627 ml. of eluant A were passed

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Table I. Analyses of Known Mixtures of Malic, Tartaric, and Citric Acids

Sample No.	Malic Acid, Mg.			Tartaric Acid, Mg.			Citric Acid, Mg.		
	Taken	Found	Error	Taken	Found	Error	Taken	Found	Error
1	17.4	17.4	0.0	20.0	20.3	+0.3	18.5	18.5	0.0
2	16.8	16.3	−0.5	22.5	22.8	+0.3	17.1	17.0	−0.1
3	16.2	16.0	−0.2	20.6	20.9	+0.3	17.5	17.3	−0.2
4	16.1	15.8	−0.3	23.0	23.0	0.0	17.4	17.3	−0.1
5	2.4	2.4	0.0	21.3	21.3	0.0	19.0	18.9	−0.1
6	15.4	15.3	−0.1	2.3	2.4	+0.1	19.8	19.8	0.0
7	16.0	15.8	−0.2	21.8	21.8	0.0	2.6	2.4	−0.2
8	0.5	0.5	0.0	21.8	21.8	0.0	19.9	19.8	−0.1
9	14.9	14.8	−0.1	0.7	0.8	+0.1	18.8	18.7	−0.1
10	18.4	18.4	0.0	22.7	22.8	+0.1	0.7	0.6	−0.1
Mean			−0.1			+0.1			−0.1

through the column at a flow rate of 0.8 cm. or 3 ml. per minute. Then, without permitting the column to drain, 500 ml. of eluant B were passed through at the same rate.

The first 377 ml. of eluate were collected in a graduated cylinder and discarded. The next three fractions of 250 ml. each were collected in volumetric flasks. Flask 1 contained all the malic acid; flask 2 contained all the tartaric acid; and flask 3 contained all the citric acid. Thus each acid was separated from the others and collected in a solution ready for the determination with permanganate.

Determination of Malic, Tartaric, and Citric Acids. Twenty-five milliliters of solution were pipetted from each flask into separate 150-ml. beakers and placed in the constant-temperature bath at 30° for 10 minutes. Then 25 ml. of standard permanganate, also at 30°, were pipetted into each beaker, and 10 ml. of 9 *M* sulfuric acid were added. Each beaker remained in the constant-temperature bath until oxidation was complete, 90 minutes for malic acid, 105 minutes for tartaric acid, and 60 minutes for citric acid. Thus each acid was oxidized completely to carbon dioxide and water.

Then 25 ml. of standard oxalic acid were pipetted into each beaker. The solutions were heated to 60° and titrated with standard permanganate from a 5-ml. buret. Thus the amount of permanganate used in the final titration was equal to the amount used to oxidize the fruit acid. Three aliquots from each elution fraction were generally analyzed in this manner.

RESULTS

Table I shows the results of the analyses of ten known mixtures of the fruit acids. In each case, the weighed acids were dissolved in 5 ml. of eluant A, transferred to the column, and treated as described above.

Table II gives the results of three analyses of one specimen of lemon juice. Analysis 1 revealed the presence of only citric acid, as reported by other investigators (*6*). Known weights of malic and tartaric acids were added to the second and third samples. The results indicate excellent recoveries of the added acids as well as high precision in the determinations of citric acid.

Table III shows the results of two analyses of the juice of Concord grapes. Good precision and accurate recovery of added citric acid are seen.

Two juices from two different batches of freestone peaches were analyzed (Table IV). The results indicate again good precision and accurate recovery of added acids. Furthermore, tartaric acid was found in both batches of peaches, although this acid has not been previously found in peaches. This is not surprising, because the concentration of tartaric acid in peaches is too small to be determined or detected by the classical procedure (*1*). It is also possible that some other acid in the peach, such as galacturonic, polygalacturonic, or gluconic, was eluted in the third fraction and therefore mistaken for tartaric acid, as the authors' investigation did not include a study of these acids.

Finally, 3.00 ml. of the grape juice and 3.00 ml. of specimen 2 of peach juice were mixed and analyzed. Table V reveals that good agreement was obtained between the quantities of acids found and the quantities expected from the results Tables III and IV.

DISCUSSION

Preliminary Elutions. Over 100 elutions were performed before the recommended conditions were selected. These preliminary elutions were done by analyzing small fractions (11 ml.) of the eluate either qualitatively or quantitatively to find the total fraction within which any one acid was contained (*4*). Dowex-1 (100- to 200-mesh) was found to be superior to Dowex-2, Amberlite IRA-400, Amberlite IRA-410, and Amberlite IR-4B for this separation. Sodium nitrate was more satisfactory than the chloride, but neither eluant alone was able to separate the three fruit acids. Attempts to achieve the separation by control of pH met with partial success. At a pH below 3, malic acid could be separated from tartaric and citric acids, whereas a pH of 9.00 gave a separation of citric acid from malic and tartaric. However, there is no pH at which a noncomplexing eluant can separate all three acids. Next, the effect of metals in the eluant as complexing agents was tried. Cadmium, aluminum, and nickel failed in this role. Finally, boric acid was tried as a complexing agent and led to the recommended method. The addition of sodium borate enabled the boric acid to serve as both complexing agent and buffer. A pH of 6.15 proved to be most satisfactory for the separation.

A concentration of 0.0800 *M* sodium nitrate (eluant A) was selected when it was found that 0.1000 *M* or more concentrated sodium nitrate failed to separate malic from tartaric acid. However, if only eluant A is used, removal of citric acid from the column would require 3050 ml. of this eluant, and the elution would last 17 hours. A considerable saving of reagents and time is gained by switching to eluant B as soon as the malic acid is removed from the column, as in the recommended procedure.

Flow rates less than the recommended value have little effect on the elution except to make it more time-consuming. Incomplete separation of malic and tartaric acids results from greater flow rates. If the sample contains more than 24 mg. of any one acid, especially malic or tartaric acid, the separation is likely to be incomplete.

Figure 1 shows a typical elution graph obtained under the recommended conditions.

The proposed procedure determines, of course, the total quantity of any given acid, both free acid and salt. For this reason, the sum of the normalities of the three acids is always slightly greater than the normality of acid determined by titration with sodium hydroxide.

Table II. Analyses of 0.300-Ml. Samples of Lemon Juice

Analysis No.	Malic Acid, Mg.		Tartaric Acid, Mg.		Citric Acid Found, Mg.
	Added	Found	Added	Found	
1	0.0	0.0	0.0	0.0	17.4
2	0.7	0.7	0.6	0.6	17.5
3	15.5	15.4	21.8	21.8	17.4

Table III. Analyses of 5.00-Ml. Samples of Grape Juice

Analysis No.	Malic Acid Found, Mg.	Tartaric Acid Found, Mg.	Citric Acid, Mg.		
			Added	Found	In juice
1	10.6	19.6	0.0	0.8	0.8
2	10.8	19.4	1.2	1.9	0.7

Table IV. Analyses of 3.00-Ml. Samples of Peach Juice

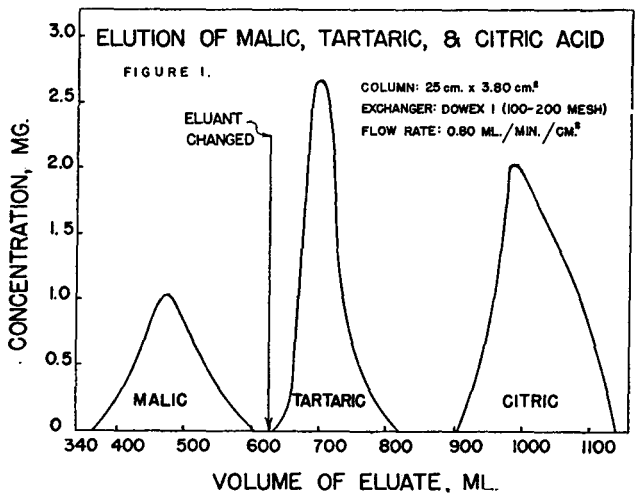
Specimen No.	Analysis No.	Malic Acid, Mg.			Tartaric Acid, Mg.			Citric Acid Found, Mg.
		Added	Found	In juice	Added	Found	In juice	
1	1	0.0	7.9	7.9	0.0	2.3	2.3	20.4
1	2	7.8	15.5	7.7	13.3	15.7	2.4	20.5
2	3	0.0	6.7	6.7	0.0	0.6	0.6	9.0
2	4	0.0	6.9	6.9	1.7	2.3	0.6	9.0

Determination of Fruit Acids by Oxidation. Under the recommended conditions of oxidation, the fruit acids react according to the following half-equations.

$$H_2C_4H_4O_5 + 3H_2O \rightarrow 4CO_2 + 12H^+ + 12e$$
$$H_2C_4H_4O_6 + 2H_2O \rightarrow 4CO_2 + 10H^+ + 10e$$
$$H_3C_6H_5O_7 + 5H_2O \rightarrow 6CO_2 + 18H^+ + 18e$$

Thus the equivalent weights of malic, tartaric, and citric acids are $^1/_{12}$, $^1/_{10}$, and $^1/_{18}$ of the molecular weights, respectively.

A large excess of permanganate is required to oxidize the fruit acids quantitatively under the recommended conditions. Therefore, it was necessary to take a one-tenth aliquot of each fraction. Thus the minimum ratio of permanganate to fruit acid in terms of equivalents was 11, and quantitative oxidation occurred in the specified times in the 30° bath. Longer periods are not desirable because of possible decomposition of the permanganate. The periods required for quantitative oxidation in a 25° bath are 120 minutes for malic acid, 165 for tartaric, and 60 for citric. The temperature of the solution rises somewhat upon the addition of 9 *M* sulfuric acid, but no steps are required to cool the mixture except to keep it in the bath.



The oxidimetric method of determining the isolated fruit acids was tested by dissolving weighed quantities of a fruit acid in 250 ml. of the appropriate eluant and then applying the recommended procedure. The average error for each acid was thus found to be ±0.1 mg.

Other Constituents of Fruit Juice. An error would be incurred in the analysis, of course, if any other reducing agent in the juice appeared in the second, third, or fourth fraction of the eluate along with the malic, tartaric, or citric acid. To investigate this point, small fractions of eluate were examined for the presence of several other possible fruit constituents, in order to find the total fraction of eluate within which the constituent was eluted under the recommended conditions. The results, summarized in Table VI, indicate that oxalic acid is the only constituent of fruit juice that is likely to interfere and that it would introduce an error in the determination of tartaric acid only. This is not serious, because oxalic acid is seldom present in fruit (*6*) and never in excess of 0.03% (equivalent to 0.1 mg. of tartaric acid per ml. of juice). Furthermore, oxalic acid can be distinguished from tartaric acid by the difference in the velocity of its reaction with permanganate.

Advantages. The proposed method is much more accurate than the classical procedure—for example, a collaborative study (*2*) indicated an average error of 3 mg. in the determination of tartaric acid in apple jelly by the traditional method, whereas the error in determination of comparable quantities by the proposed method is about 0.1 mg. Furthermore, the proposed method is much more rapid. The classical procedure for the determination of any one of the major fruit acids requires about 2 days; but all three acids can be determined by the proposed method in 7.5 hours, during only 3 of which the operator's attention is required.

Table V. Analysis of Mixture of Grape and Peach Juices

	Malic Acid, Mg.	Tartaric Acid, Mg.	Citric Acid, Mg.
In 3.00 ml. of grape juice	6.4	11.7	0.5
In 3.00 ml. of peach juice	6.8	0.6	9.0
Total expected	13.2	12.3	9.5
Found	13.3	12.4	9.7
Difference	+0.1	+0.1	+0.2

Table VI. Elution of Other Fruit Constituents

Constituent	Ml. of Eluate Containing Constituent
Common sugars	23- 91
Succinic acid	91- 148
Lactic acid	68- 240
Malic acid	383- 610
Tartaric acid	645- 793
Oxalic acid	690- 850
Citric acid	907-1100

A minor disadvantage stems from the nonuniformity of commercial ion exchange resins. A different batch of Dowex-1 (100- to 200-mesh) might have slightly different properties and hence require slight changes in the elution conditions. It is advisable, therefore, to test each column of Dowex-1 before using it for this determination by running separate elutions of known quantities of malic, tartaric, and citric acid. In each case, small fractions of the eluate should be analyzed in order to determine the limits of eluate within which each acid is contained.

ACKNOWLEDGMENT

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Colorimetric Microdetermination of Boron by the Curcumin-Acetone Solution Method—Correction

In the article on "Colorimetric Microdetermination of Boron by the Curcumin-Acetone Solution Method" [Silverman, Louis, and Trego, Katherine, ANAL. CHEM., 25, 1264 (1953)] at the bottom of the first column on page 1265 the last sentence under "Stock Boron Solution" should read: One milliliter equals 0.1 mg. of boron.

LOUIS SILVERMAN

Titrimetric Determination of Thorium

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Comparatively few volumetric methods for thorium are available; those involving precipitation of thorium with oxalate, iodate, or molybdate are indirect and subject to coprecipitation errors. A proposed method consists of direct titration of thorium with the disodium salt of ethylene-diaminetetraacetic acid, a soluble complex being formed. An internal indicator gives a sharp, reversible color change at the end point. Stoichiometric results are obtained in the pH range 2.3 to 3.4. Using Alizarin Red S indicator, no interference is caused by lithium, sodium, potassium, magnesium, calcium, strontium, barium, lanthanum, chromium, manganese, cobalt, silver, zinc, cadmium, or uranyl ions. The following ions interfere, either by forming stable Versene complexes or by reacting with the indicator: titanyl, zirconyl, cerium(III), vanadyl, iron(III), nickel, copper(II), tin(II, IV), lead, and bismuth. Levine and Grimaldi have shown that extraction with mesityl oxide separates thorium from all metals except zirconium, uranium, and vanadium. When this extraction is followed by a Versene titration, the result is a rapid and widely applicable analytical method for thorium.

BECAUSE of its colorless nature and single valence state, few volumetric methods are available for the determination of thorium. Most of the proposed methods involve precipitation and filtration of a thorium salt, followed by determination of either the acid radical of the salt or the excess precipitating reagent. Examples are the iodometric determination of iodate in thorium iodate (*9, 10*), titration of thorium oxalate with permanganate (*5*), and oxidimetric determination of thorium molybdate after reduction of the molybdenum to the trivalent state (*1*). Blaedel and Malmstadt (*2*) developed a method for thorium, using a high frequency titrator to determine the end point. The solution to be analyzed is added to a known excess of oxalate and the remaining oxalate is titrated with a standard thorium nitrate solution. Amperometric titration of thorium with molybdate has been reported by Smales and Airey (*11*) and by Gordon and Stine (*6*). Deshmukh and Swamy reported a titrimetric method involving selenious acid (*3*).

The present method consists of a direct titration of thorium with a standard solution of disodium ethylenediaminetetraacetate (Versene), a soluble complex being formed. [Apparently a similar method for thorium is being studied independently by ter Haar of Eindhoven, Holland. Brief mention of this was made in the oral "discussion" of another paper (*7*). This information reached the authors after this paper had been submitted for publication.] An internal indicator gives a sharp, reversible color change at the end point. The titration is carried out in acid solution where comparatively few cations form Versene complexes of sufficient strength to cause interference. Thorium can be conveniently separated from most interfering cations and anions by a preliminary extraction with mesityl oxide (*8*). When this separation is followed by a Versene titration, the result is a rapid and widely applicable analytical method for thorium.

REAGENTS AND SOLUTIONS

Alizarin Red S. Dissolve 0.05 gram of sodium alizarin sulfonate in 100 ml. of water.

Chrome Azurol S. Dissolve 0.05 gram of Chrome Azurol S in 100 ml. of water.

Thorium Nitrate. Prepare a 0.025 *M* solution by dissolving about 13.8 grams of reagent grade thorium nitrate tetrahydrate in 1 liter of 0.02 to 0.03 *M* nitric acid. Standardize the solution gravimetrically by precipitation as thorium oxalate followed by ignition to the oxide.

Versene. Prepare a 0.025 *M* solution by dissolving 9.3 grams of reagent grade disodium dihydrogen Versenate (the disodium salt of ethylenediaminetetraacetic acid) in water and diluting to 1 liter. Standardize the solution against primary standard calcium carbonate using the procedure described by Goetz, Loomis, and Diehl (*4*).

PROCEDURE

For moderately small amounts of thorium use a 10-ml. buret. Take a sample containing 6 to 50 mg. of thorium and adjust the volume to about 25 ml. Add 4 drops of Alizarin Red S indicator and adjust the acidity with dilute ammonia until a definite pink color appears (about pH 2.5). Then titrate with standard 0.025 *M* Versene until the color begins to fade rapidly. Adjust the pH to 3.0 using a pH meter and continue the titration. The end point has been reached when the last trace of pink disappears, giving a clear yellow color. Magnetic stirring adds to the convenience of the titration.

For larger amounts of thorium, take a sample containing 0.12 to 0.24 gram of thorium in a volume of about 100 ml. Add 6 drops of indicator and titrate as described above, using a 50-ml. buret.

The procedure for extraction with mesityl oxide is given by Levine and Grimaldi (*8*). Collect the aqueous layers stripped from the mesityl oxide after the extraction in a 50-ml. volumetric flask and dilute to volume. Withdraw a 5- or 10-ml. aliquot and titrate with Versene, using the procedure described above.

Calculations

$$\text{Mg. of Th} = 232.1\ VM$$

where V = volume of Versenate solution and M = molarity of Versenate solution.

INDICATOR

Several substances form colored complexes with thorium and can be used as indicators in the Versene titration. Among these are Alizarin Red S, Chrome Azurol S, carminic acid, Thorin, and ammonium purpurate. Of these, Alizarin Red S is recommended because it gives sharper end points and fewer cations interfere.

EFFECT OF PH

Alizarin Red S is an acid-base indicator (transition range 3.8 to 5.0). As the color of its basic form and that of the thorium complex are almost identical, Alizarin Red S can function as an indicator for thorium only in solutions having a pH of 3.8 or less. The intensity of the thorium–Alizarin Red S color decreases rapidly with increasing acidity, starting at about pH 2.1. This sets a lower pH limit for the titration somewhere in the neighborhood of pH 2.1.

A study was made of accuracy as a function of pH. The results (shown in Figure 1) indicate that the titration is stoichiometric in the pH range 2.3 to 3.4 (thorium hydroxide begins to precipitate around pH 3.5). The sharpest color change was found around pH 2.8.

In the above titrations a 1 to 1 thorium-Versene complex is formed. Two moles of hydrogen ions per mole of thorium are

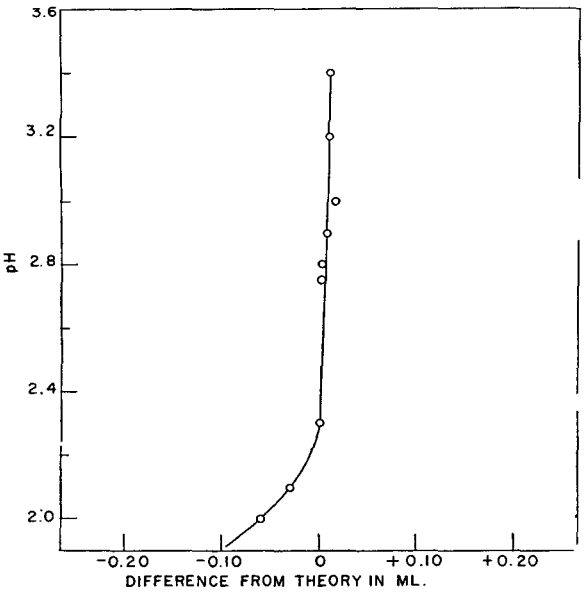


Figure 1. Effect of pH on Accuracy

released during the titration. This causes some difficulty, as the final pH must be in the range 2.3 to 3.4. Use of a buffer (such as sodium chloroacetate–chloroacetic acid or sodium bicarbonate–sulfanilic acid) is obvious, but the authors have found that buffers often decrease the sharpness of the end point and cause erratic results. By keeping the thorium within a given concentration range and by adjusting the pH near the end point, the above procedure gives accurate results without the use of a buffer.

INTERFERENCES

Foreign cations may interfere by forming stable Versene complexes or by forming colored complexes with the indicator. If a cation forms no colored complex with the indicator, its interference is determined by the stability of its Versene complex relative to the thorium-Versene and the thorium-indicator complexes. To prevent interference, the Versene complex of the metal in question must be weaker than either the thorium-Versene or thorium-indicator complex.

Table I correlates cation interferences with the formation constants of their Versene complexes. In addition to those listed, titanium, zirconium, cerium, vanadium, tin, and bismuth also interfere. By changing to Chrome Azurol S indicator, thorium can be titrated successfully in the presence of cerium(III), although the others still interfere. Potassium, strontium, chromium, silver, and uranium do not interfere. Although chromium(III) forms a very stable Versene complex ($K = 10^{24}$), it does not interfere because of the very slow rate of complex formation. Approximately 0.01 M concentrations of aluminum do not interfere, provided the pH at the end point is around 2.4 or 2.5. If very large amounts of aluminum are present, some preliminary separation is required. If uranium is present, some dilution may be required before titration.

Zirconium and most of the other interfering cations cause a delayed and indistinct end point but do not interfere quantitatively. A method is now being developed, however, which should extend the Versene titration to the quantitative determination of zirconium.

Table I. Interference Study[a]

Metal	Versene Complex, Log Form, K
No Interference	
Na^+	1.66
Li^+	2.79
Ba^{++}	7.76
Mg^{++}	8.69
Ca^{++}	10.59
Mn^{++}	13.47
La^{+++}	15.4
Co^{++}	16.10
Cd^{++}	16.48
Zn^{++}	16.58
Interfering Ions	
Pb^{++}	18.2
Cu^{++}	18.38
Ni^{++}	18.45
Fe^{+++}	25.

Conditions. 29 mg. of thorium titrated in presence of 5 to 15 mg. of foreign cations. Indicator. Alizarin Red S.
[a] Some additional interfering and noninterfering ions are discussed in the text.

Table II. Titration of Thorium with Disodium Versenate

Th Taken, Mg.	Added Impurity, Mg.	Versene, Ml.	Theoret. Versene, Ml.	Diff., Ml.
34.3	None	4.99	4.98	+0.01
68.5		9.97	9.96	+0.01
11.4		1.99	1.99	+0.00
114.0		19.42	19.44	−0.02
142.7		24.35	24.32	+0.03
34.3	Ca^{++} 6	4.96	4.96	±0.00
34.3	Zn^{++} 5	4.98	4.96	±0.02
34.3	Mn^{++} 5	5.00	4.98	±0.02
28.8	Al^{+++} 2	5.16	5.16	±0.00
28.8	Al^{+++} 7	5.20	5.16	+0.04
28.8	Al^{+++} 34	5.25	5.16	+0.09
28.8	UO_2^{++} 25	5.16	5.16	+0.00
28.8	UO_2^{++} 25	5.17	5.16	+0.01

Table III. Titration of Thorium Solutions Recovered by Extraction

Aliquot, Ml.		Versene, Ml.	Theoret. Versene, Ml.	Diff., Ml.
5.00	(14.6 mg. Th)	2.49	2.49	±0.00
10.00		4.99	4.97	+0.02
5.00		2.48	2.49	−0.01
5.00		2.49	2.49	±0.00
10.00		5.01	4.97	+0.04
10.00		4.96	4.97	−0.01
5.00		2.53	2.49	+0.04
5.00		2.51	2.49	+0.02

Anions which form precipitates or complexes with thorium cannot be tolerated. Among these are phosphate, fluoride, oxalate, sulfate, and mandelate. Small amounts of acetate do not interfere, but larger concentrations cause a poor end point and low results.

Levine and Grimaldi (*8*) have recently developed an excellent extraction method for the isolation of thorium. An aqueous thorium solution is made 1.2 M in nitric acid and 19 grams of aluminum nitrate nonohydrate per 10 ml. are added as a salting out agent. This solution is then extracted with mesityl oxide, thorium nitrate passing quantitatively into the organic layer in one extraction. Determination of the thorium content of this extract by Versene titration is entirely feasible.

This procedure is particularly noteworthy because it separates thorium from rare earths and from large amounts of fluoride and phosphate. Only zirconium, uranium, vanadium, and small amounts of aluminum accompany thorium in the extraction. Of these, uranium and aluminum do not interfere with the Versenate titration of thorium. Zirconium and vanadium can usually be removed prior to the extraction of thorium.

PRECISION AND ACCURACY

The Alizarin Red S end point is usually very sharp and can be determined with an estimated maximum error of ±0.01 ml. using the small buret or ±0.05 ml. using a 50-ml. buret. The presence

of certain cations makes the end point slightly less vivid and may therefore reduce the accuracy slightly. For example, if aluminum is present, the color change at the end point is from red to pale orange; in the absence of aluminum a pink to yellow change is observed. Table II gives typical data obtained in the titration of thorium. Data for the recovery of thorium by mesityl oxide extraction and versene titration are given in Table III.

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Determination of Calcium in Biological Material by Flame Photometry

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Calcium determinations in biological material by flame photometry at 620 mμ are convenient, rapid, and reliable. Phosphate suppresses the calcium emission, and protein partially prevents the action of phosphate. Studies to determine when correction must be made for phosphate inhibition are reported. Procedures are given for determination of calcium in blood serum, serum ultrafiltrate, and urine.

THE use of flame photometry for the clinical determination of sodium and potassium has become common practice. This technique, however, has not yet displaced the classical methods for estimating calcium by oxalate precipitation.

The emission spectrum of calcium is relatively weak and therefore is especially subject to interference by the presence of strong emitters such as sodium or potassium. In addition, certain anions such as phosphate (*4*, *7*) lower the intensity of the emission spectrum.

In the present investigation, a number of the variables encountered in the determination of calcium in biological samples have been studied in detail. With certain precautions, the flame photometric method has proved convenient, rapid, and reliable.

METHODS, MATERIALS, AND EQUIPMENT

The instrument used was a Weichselbaum-Varney flame photometer equipped with an RCA 1P 21 photomultiplier tube and supplied with city gas passed through two ballast tanks to minimize fluctuations in pressure. Although highest readings were obtained at 556 mμ, the background was also high and more reproducible results could be obtained at 620 mμ. Even at this wave length the sensitivity was sufficient to permit the direct determination of calcium in diluted serum and urine, obviating time-consuming procedures such as protein precipitation, precipitate washing, and acid-ashing.

In determining calcium, the meter is adjusted to zero after a solution containing all the ions except calcium has been placed in the atomizer. The 100% adjustment is made using a solution with a known calcium content—e.g., 2 p.p.m.—and selecting the proper sensitivity range. The unknown solution is then placed in the atomizer, and the per cent of the 100% value read on the meter—e.g., 75% of 2 p.p.m. = 1.5 p.p.m.—gives the calcium content. The authors' experience with calcium has been that the scale is linear with respect to the calcium content of the solution when all other variables are held constant. In the case of an ion that did not give a linear response, it would be necessary to construct a calibration curve by using a number of solutions of different known ion content.

Inorganic phosphate in trichloroacetate filtrates and total phosphate in wet-ashed (concentrated sulfuric acid and 30% hydrogen peroxide) specimens were determined by the method of Fiske and Subbarow (*3*).

The ultrafiltrate of serum was prepared using the apparatus of Toribara (*6*).

EFFECT OF ALKALI CATIONS

Sodium. As shown in Figure 1, both the blank and sample readings increase linearly with increasing sodium concentration. Therefore, for routine analyses, the sodium level must be maintained at some fixed value. Weichselbaum (*1*, *2*) has suggested a level of 5 meq. of sodium per liter and this concentration is conveniently and accurately attained by addition of sodium chloride to 1 to 100 dilutions of blood and serum ultrafiltrate, on the assumption that the original samples contain 150 meq. per liter. This assumption introduces negligible error. With urine and other specimens containing variable amounts of sodium, preliminary determinations of this alkali must be made to determine the quantity of sodium chloride to be added to give a final dilution of 5 meq. per liter.

Potassium. The effect on a calcium solution is shown in Figure 2. The potassium emission at 620 mμ is 2.0 times that of an equivalent amount of sodium when no calcium is present. In 1 to 100 dilutions of blood serum, or serum ultrafiltrate, so little potassium is present (0.04 to 0.06 meq. per liter) that the determination of calcium is not seriously affected. However, the concentration of potassium in urine is sufficiently high and variable to be of significance. The correction factor may be determined on the basis of an equivalent sodium effect by multiplying the potassium content by 2.0.

EFFECT OF PHOSPHORUS

The depression of the emission spectrum of calcium by the presence of inorganic phosphate has been reported (*4*, *7*). This inter-

Table I. Effect of Phosphate on Serum and Ultrafiltrate

Phosphorus Added, P.P.M.	Apparent Calcium, P.P.M.[a] (1:100 Dilution)			
	Direct Dilution[b]		Oxalate Precipitate[c]	
	Serum	Ultrafiltrate	Serum	Ultrafiltrate
0	1.03	0.54	1.01	0.64
1.68	1.02	0.51	0.85	0.52
16.8	0.80	0.54	0.85	0.54

[a] Read against standards containing no phosphate.
[b] Diluted serum already contained 2.08 p.p.m. total and 0.48 p.p.m. inorganic phosphorus. Diluted ultrafiltrate contained 0.54 p.p.m. total and 0.49 p.p.m. inorganic phosphorus.
[c] Oxalate precipitate contained no phosphate except that which was added.

ference has been confirmed, but the action of phosphate has proved to be complex and is modified by a number of factors. Representative data are presented in Figure 3. The addition of increasing amounts of inorganic phosphate to a solution of calcium chloride (1 p.p.m. of calcium) in distilled water gave decreasing emission readings and the maximum inhibition of about 25% was reached at a level of about 1 p.p.m. of phosphorus (calcium-phosphorus ratio of 0.775). Similarly, the addition of ester phosphate (sodium β-glycerophosphate) also reduced the reading given by 1 p.p.m. of calcium, but greater quantities of organic phosphorus were required to produce both just detectable and also maximal spectral inhibition.

In biological solutions, the presence of protein prevents, in part, the inhibitory action of phosphate. Therefore, an extremely large amount of phosphate must be added to serum to cause any depression of the calcium emission, whereas the absence of protein in ultrafiltrate allows maximum suppression with the phosphate normally present (no further depression is caused by addition of phosphate). This is shown in Table I, where a comparison is made between calcium isolated from the ultrafiltrate by alkaline precipitation of the oxalate and that determined directly. In urine, too, there is sufficient inorganic phosphate to give maximal suppression of readings, as shown by the following experiment.

A urine sample diluted 1 to 100 contained 2.25 meq. per liter of sodium, 0.95 meq. per liter of potassium (total alkali effect in terms of sodium = 2.25 + 2 × 0.95), and 7.3 p.p.m. of phosphorus. After the sodium effect had been adjusted to 5 meq. per liter, uncorrected analysis, using pure solutions as standards, a calcium content of 175 p.p.m. of undiluted urine was given. When the calcium was precipitated by the addition of ammonium oxalate, dissolved, and then determined by the flame photometer, a value of 236 p.p.m. of undiluted urine was obtained. The calcium emission in the urine sample was depressed 26%, the same depression obtained when phosphate is added to a solution of calcium.

The partial prevention of phosphate suppression by protein as shown in Table I and Figure 3 was further demonstrated. In Table II are the results obtained before and after precipitation of the proteins by trichloroacetic acid. Here, removal of protein resulted in phosphate inhibition and much lower readings. Insignificant amounts of calcium were carried down in the protein precipitate. The effect of trichloroacetic acid, in the concentrations used, on the spectrum of a calcium chloride solution was negligible.

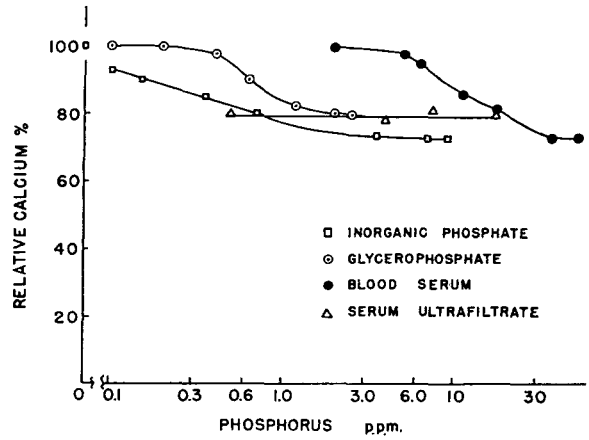


Figure 3. Effect of Phosphorus on Calcium Emission at 620 Mμ under Various Conditions

The reverse experiment was also conducted. By shaking 25 ml. of serum for 3 days with the sodium form of a cationic exchange resin, Dowex 50, the calcium content was reduced to 8 p.p.m. Some of the serum was also treated with ammonium oxalate to remove calcium. The samples for analysis were 1 to 100 dilutions of these sera containing 1 p.p.m. of added calcium, and 0, 0.84, or 1.68 p.p.m. of added phosphorus. In all cases, the flame photometer indicated a calcium content of 1.06 p.p.m., showing that serum protein prevents the spectral inhibition of phosphate.

As a confirmatory test, a known protein was added to solutions of calcium and phosphorus. A 4% aqueous solution of Armour's crystallized bovine albumin, treated with ammonium oxalate, contained 6 p.p.m. of calcium. Samples for analysis were 1 to 100 dilutions of this solution containing added calcium and phosphorus. The results, given in Table III, again show the protection against phosphate inhibition given by protein.

NONINTERFERING IONS

Table IV shows the noninterfering ions. In concentrations up to 20 times that present in serum diluted 1 to 100, they produce no detectable effect on the calcium emission.

The first figure represents an approximation of the concentrations most likely to be encountered in routine analyses.

RECOMMENDED ANALYTICAL PROCEDURE

Because the proteins in serum eliminate the quenching by the usual concentrations of phosphate, analysis by flame photometry may be carried out directly on diluted serum; attention to the sodium effects is, of course, necessary.

In serum ultrafiltrate, correction for phosphate quenching is usually necessary, either by using

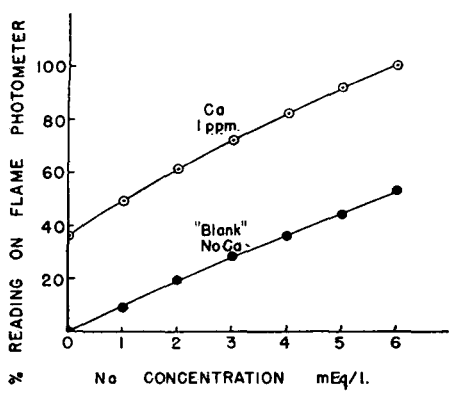


Figure 1. Variation of Emission at 620 Mμ with Sodium Concentration

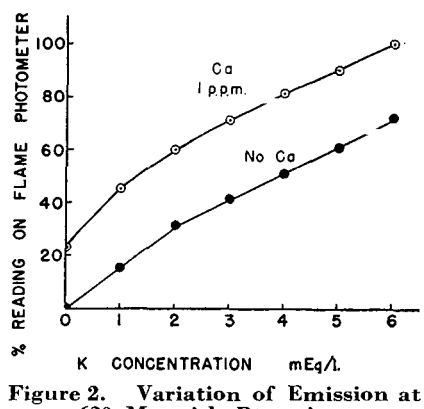


Figure 2. Variation of Emission at 620 Mμ with Potassium Concentration

Table II. Effect of Protein Removal

	Apparent Calcium, P.P.M. (1:100 Dilution)
Serum	1.00
Trichloroacetic filtrate	0.72
Trichloroacetic filtrate + 2.1 p.p.m. P	0.72
Trichloroacetic filtrate + 8.4 p.p.m. P	0.72
Trichloroacetic filtrate + 16.8 p.p.m. P	0.72
Trichloroacetic filtrate + 33.6 p.p.m. P	0.72
Ashed protein precipitate	0.008

Table III. Effect of Albumin and Phosphorus

Phosphorus, P.P.M.	Apparent Calcium, P.P.M.	
	With albumin	No albumin
0	1.10	1.00
1.68	1.00	0.80
3.36	0.98	0.80

Table IV. Noninterfering Ions

	Ion, P.P.M.
Oxalate	0.05– 1.0
Sulfate	0.3 – 6.0
Ammonium	1.8 – 36
Bicarbonate	6.0 –120

predetermined factors or the addition of phosphate to comparable standards.

Calcium in urine is most conveniently determined by first isolating as the oxalate to eliminate all interferences and correction factors.

Reagents. Stock Calcium, 1.00 mg. per ml. Dissolve 2.4970 grams of Iceland spar in a minimum volume of dilute hydrochloric acid and dilute to 1000 ml. with distilled water.

Substock Calcium. Dilute 10 ml. of stock solution to 1000 ml. The substock calcium concentration is 10 p.p.m.

Sodium Chloride, 100 meq. per liter. Dissolve 5.845 grams of dried reagent grade sodium chloride and dilute to 1000 ml. of solution.

Sterox. Dissolve 5 grams of Sterox SE (Monsanto) in 500 ml. of water. A touch of caprylic alcohol on the end of a stirring rod can be used to break up the foam incurred in preparing this solution or any of the subsequent solutions.

Calcium Standards. In 500-ml. volumetric flasks, place 25 ml. of sodium chloride solution, 10 ml. of Sterox solution, and calcium substock to obtain on dilution the desired calcium concentration. Working concentrations are 0 to 2 p.p.m. of calcium. Prepare similar phosphate-containing standards by effecting a 1 p.p.m. concentration of phosphorus with diammonium hydrogen phosphate.

Calcium Sterox. Dissolve 5.117 grams of dried reagent grade sodium chloride in a 500-ml. volumetric flask with 5 grams of Sterox and dilute to volume. One milliliter of this solution diluted to 50 ml. (2% solution) has a concentration of 3.5 meq. per liter of sodium.

Calcium Sterox 2. Dilute 143 ml. of the above solution to 500 ml. with distilled water. A tenfold dilution of this solution has a concentration of 5.0 meq. per liter of sodium.

Procedure. Blood Serum. Dilute 0.5 ml. of serum and 1 ml. of calcium Sterox to 50 ml. Read against standards containing no phosphorus.

Serum Ultrafiltrate. Dilute the same as serum, but read against the standards containing phosphorus (1 p.p.m.). An alternative method is to read the diluted ultrafiltrate against the working standards used in the serum analysis and then correct for phosphate quenching, using a predetermined phosphate quenching curve similar to Figure 3. The reading will be raised about 25% after correction.

URINE, Method 1. Place 1 to 5 ml. of acidified urine (add concentrated hydrochloric acid to a yellow color of bromocresol green) in a 15-ml. conical centrifuge tube. Add 2 ml. of saturated ammonium oxalate and ammonia until a green color is obtained and allow to precipitate for several hours. Centrifuge and carefully aspirate off the supernatant liquid. Wash the precipitate once by adding 2 ml. of 2% ammonia, followed by centrifugation and careful aspiration.

Dissolve the precipitate in a few drops of dilute hydrochloric acid and transfer to a volumetric flask. The size depends on the amount of precipitate. Usually 10 times the volume of the urine sample is a good first approximation. Wash all the dissolved calcium carefully into the volumetric flask and dilute to volume with distilled water. Dilute aliquots of this solution 1 to 10 or 1 to 20 for flame photometric readings, making certain that all final dilutions contain 5 meq. of sodium per liter (10% calcium Sterox 2).

Method 2. If only a small amount of sample is available, or if sodium and potassium as well as calcium are to be determined, an alternative method can be used. In this procedure acidified diluted urine is read directly on the flame photometer.

First determine the sodium and potassium concentrations of the acidified urine. Calculate the milliequivalents per liter of sodium and potassium present when the urine is diluted 1 to 100 or 1 to 200. Using one of these dilutions, add sufficient calcium Sterox 2 to bring the final concentration of sodium plus 2.0 times potassium to 5 meq. per liter. Compare on the flame photometer against standards containing 1 p.p.m. of phosphorus or read against standards containing no phosphorus and correct by a predetermined phosphate quenching curve similar to Figure 3.

DISCUSSION

The direct determination of the calcium content of diluted serum and serum ultrafiltrate requires only a small (0.5-ml.) sample. The potassium content of the serum is so low that it does not lead to serious errors (about +2%) and the sodium concentration is constant enough to allow easy compensation.

Because of the great variability of concentrations of sodium and potassium in urine and the availability of large amounts of sample, Method 1, involving a preliminary oxalate precipitation, is preferred to the direct dilution technique. This step removes the interfering sodium, potassium, and phosphate ions. While it has been shown spectrographically (*5*) that ordinarily about 10 to 15% of the oxalate precipitated at pH 5 is due to magnesium, the presence of magnesium will not interfere with the flame photometric procedure. Extensive washing of the precipitate is unnecessary, as oxalate does not interfere. As long as all the calcium is precipitated, dissolved, and quantitatively transferred, the results will be accurate. The analysis of specimens of urine containing albumin or protein would be difficult to evaluate if the direct method were used and, in such a case, the oxalate precipitation method would be almost mandatory.

For precise measurements, making frequent alternating readings of standard and unknown will give a precision of ±1% as claimed by Weichselbaum (*1*) for this instrument. In routine laboratory analysis ±3 to 4% is easily obtained. The accuracy of the method is of the same order as the precision, as it is a direct comparison method in which readings of an unknown are compared with a standard calcium solution.

Despite the interference problems encountered in the flame photometric determination of calcium, the procedure still remains rapid, accurate, and sensitive. In many respects flame photometry surpasses the conventional methods of calcium determination.

ACKNOWLEDGMENT

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Quantitative Determination of Methyl Mercaptan, Dimethyl Disulfide, and Dimethyl Sulfide in a Gas Mixture

Following Separation of Mercaptan by Mercuric Cyanide and Absorption of Disulfide and Sulfide in Benzene

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Studies were undertaken to determine the sulfur products of microbial decomposition of organic sulfur compounds. Evidence was obtained that volatile sulfur products such as methyl mercaptan and alkyl sulfide were produced from methionine. No satisfactory methods were available for the quantitative determination of these products, formed slowly during the decomposition process. The method described provided a means of quantitatively determining methyl mercaptan, dimethyl disulfide, and dimethyl sulfide occurring as mixtures in gas. The gas was passed through mercuric cyanide and benzene. Methyl mercaptan was removed by the mercuric cyanide, whereas dimethyl disulfide and dimethyl sulfide were removed by the benzene. The immediate value of the method was the solution of the difficult problem of determining the volatile products of methionine decomposition. Similar organic compounds are encountered in products of the brewing industry, in petroleum products, in sewage, and in various other substances undergoing microbial attack. The method should find application where quantitative determination of mercaptans and alkyl sulfides is needed.

In a study of the transformation of methionine by microorganisms it was found that all of the sulfur of methionine was converted to organic sulfur products that volatilized from the culture solution. The use of 3% mercuric cyanide and 4% mercuric chloride as trap solutions for the absorption and precipitation of these volatile sulfur products as mercury derivatives, as described by Challenger and Charlton (*4*), indicated that methyl mercaptan (methanethiol) and dimethyl disulfide, and possibly dimethyl sulfide, were present. These reagents were inadequate for the quantitative separation and determination of the highly volatile sulfur compounds because the mercury derivatives could not be analyzed accurately. A review of the literature revealed no method for the quantitative determination of a mixture of methyl mercaptan, dimethyl disulfide, and dimethyl sulfide, slowly volatilizing from a bacterial culture solution over a period of several days. The methods either could not be applied to the conditions of the bacterial system, or could not be applied to a gas mixture of these three types of compounds.

Some parts of methods used in the petroleum industry for the determination of mixtures of organic sulfur compounds in hydrocarbon solutions (*1, 2, 5, 6, 11*) were found to be adaptable to the conditions of a constant gas flow of volatile sulfur products. Indeed, the analytical procedure of Bell and Agruss (*2*), whereby organic sulfides are dissolved in benzene and determined in this solvent, was incorporated in the adopted procedure.

APPARATUS AND SEPARATION PROCEDURE

An air stream containing the volatile products released from the culture solution in the 250-ml. Erlenmeyer flask, *A* (Figure 1), was drawn at the rate of approximately 5 liters per hour through 175 ml. of 4% mercuric cyanide in absorption bottle *B* and 50 ml. in test trap *C*, which absorbed the mercaptan. Then it passed through 175 ml. of benzene in absorption bottle *D*, which absorbed the dimethyl sulfide and dimethyl disulfide. The reflux condenser, *E*, was cooled with iced water, 5, to keep the temperature between 5° and 15° C. and prevent appreciable loss of benzene (loss was from 10 to 15 ml. a day). The iced water jacket was insulated with a 40-mm. layer of asbestos, 6. The jacket was drained at 7 and iced water was added as needed. Even when the room temperature was 30° C. the temperature of the water did not rise above 15° C. in an 8-hour period.

The glass wool in the condenser, 4, was kept saturated with benzene by slowly releasing the solvent from the separatory funnel, *F*, and this served to trap any of the sulfides that were not collected in *D*. The stopcock of the separatory funnel was lubricated with silicone lubricant. Attached to the end of the separatory funnel by benzene-resistant plastic tubing was glass tubing reaching part way into the glass wool. From the condenser the air stream was drawn through absorption bottle *G*, which contained 175 ml. of 3% mercuric chloride that served as a test trap to collect any mercaptan, dimethyl disulfide, or dimethyl sulfide that passed through the system. In no case were any of these products detected in this solution.

The reflux system was required because of the volatility of benzene. In tests made without the reflux condenser but with the benzene in the absorption bottle kept at 5° C. to prevent excessive loss by volatilization, there was incomplete absorption of the sulfur products.

Before the solution of mercuric cyanide was adopted as the absorbent for mercaptan, tests were made in which standard 0.05 *N* silver nitrate was used as the absorbent. This solution preceded absorption bottle *G*, and *B* and *C* were eliminated. Part of the methyl mercaptan was recovered in the benzene and part in the solution of silver nitrate. After absorption, the excess silver nitrate was determined by titration with standard ammonium thiocyanate, ferric alum being used as the indicator. The use of mercuric cyanide to absorb the methyl mercaptan was preferable because a standard solution was not required, and the standard silver nitrate was unstable. Furthermore, the silver precipitate of methyl mercaptan is fine, clings to the glass, and decomposes readily with no distinct melting point, whereas the precipitate formed by mercuric cyanide, mercuric dithiomethoxide, can be readily collected, dried, and weighed, and has a specific melting point of 175° C.

Mercuric cyanide is inert to dimethyl disulfide and dimethyl sulfide, and the solution absorbed all of the mercaptan from the air stream. It was, therefore, unnecessary to test for mercaptan in the benzene absorbent or to remove mercaptan from the solvent before making the determinations for the sulfides.

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REAGENTS

Reagent-grade chemicals were used throughout. The methyl mercaptan, dimethyl disulfide, and dimethyl sulfide were Eastman chemicals.

Ferric alum indicator. Eighty grams of ferric alum were dissolved in 400 ml. of 4 *N* nitric acid and made to 800 ml.

Alcoholic plumbite. A solution of sodium hydroxide (25%) was saturated with lead monoxide and filtered, and 100 ml. of the clear filtrate were mixed with 100 ml. of ethyl alcohol (95%).

METHODS

The methyl mercaptan was absorbed in the solutions of mercuric cyanide. Tests for the methyl mercaptan were made separately on the contents of containers *B* and *C*. The precipitate of mercuric dithiomethoxide was filtered off on No. 42 Whatman filter paper, washed, and dried in vacuum over calcium chloride to constant weight. The filtrate and washings were collected in a 200-ml. volumetric flask. The amount of methyl mercaptan was calculated from the weight of the precipitate, assumed to be mercuric dithiomethoxide, $(CH_3S)_2Hg$. A portion of the precipitate was recrystallized from ethyl acetate three times and the melting point as well as the mixed melting point with authentic mercuric dithiomethoxide was determined. The compound turns greenish brown at 160° C. and melts at 175° C. with decomposition.

A portion of the precipitate was transferred to a boiling flask provided with a ground-glass stopper carrying a separatory funnel and a tube leading to an absorption vessel containing standard 0.01*N* iodine, which in turn was connected to a similar vessel containing standard 0.01*N* sodium thiosulfate. Concentrated hydrochloric acid (25 ml.) was added from the separatory funnel and the solution was heated and boiled for 20 minutes, the liberated mercaptan being absorbed by the iodine. The amount of mercaptan was calculated from the decrease in iodine by thiosulfate titration, and was also estimated indirectly by measuring the cyanide released by reaction of methyl mercaptan with the mercuric cyanide to form mercuric dithiomethoxide (*8*).

The filtrate and washings from the precipitate of mercuric dithiomethoxide were made to 200 ml., and 50-ml. aliquots were treated with 5 ml. of 0.3*N* mercuric nitrate, 5 ml. of 4*N* nitric acid, and 1 ml. of ferric alum indicator, and titrated with standard 0.1*N* ammonium thiocyanate (*7*). The mercuric nitrate reacts with the cyanide released from the mercuric cyanide in the absorbing solution by the mercaptan and forms mercuric cyanide. The mercury of the residual mercuric nitrate was titrated.

Because mercuric cyanide is much less dissociated than mercuric thiocyanate, the results are unaffected by mercuric cyanide. The method was also verified by titration of solutions of mercuric cyanide to which measured amounts of methyl mercaptan had been added, and by the gravimetric and iodometric determinations of the mercury precipitates. Mercuric cyanide proved to be a particularly desirable reagent for absorption of methyl mercaptan, for it was possible to determine mercaptan, after absorption by gravimetric and iodometric determinations of the precipitate and by the titrimetric determination on the residual solution. It was not necessary to use a standard solution of mercuric cyanide in the absorbing vessels.

Dimethyl disulfide and dimethyl sulfide were determined on the benzene absorbent. The general pattern of the analytical scheme of Bell and Agruss (*2*) was followed, but modifications of Faragher, Morrell, and Monroe (*6*) and of Ball (*1*) were adopted.

Condenser *E* was washed with benzene into the absorption bottle, *D*, and the benzene was made to 200 ml. in a volumetric flask. At this point two methods of analysis were used to determine dimethyl disulfide and dimethyl sulfide.

Scheme A. To a 100-ml. aliquot in a 250-ml. Erlenmeyer flask were added 25 grams of powdered zinc and 50 ml. of glacial acetic acid. The flask was immediately attached to a reflux condenser equipped at the top with a trap containing 20 ml. of standard 0.05*N* silver nitrate diluted to 50 ml. and the solution was heated and refluxed for 3 hours. The dimethyl disulfide was thereby reduced to methyl mercaptan. After cooling, the flask was removed and the contents and washings were transferred to a 500-ml. separatory funnel. The water layer was drawn off and discarded and the benzene layer was washed with distilled water until the washings were no longer acid to litmus, after which the benzene was filtered and the volume made to 200 ml.

Determinations were made on 50-ml. aliquots for methyl mercaptan formed from the dimethyl disulfide, according to the method of Borgstrom and Reid (*3*) modified by *Malisoff and Anding* (*9*). The aliquot was transferred to a 250-ml. glass-stoppered flask and an excess (usually 25 ml.) of 0.05*N* silver nitrate, 10 ml. of ferric alum indicator, and 3 ml. of 95% ethyl alcohol were added. After being vigorously shaken, the solution was titrated with standard 0.05*N* ammonium thiocyanate to the end point, which was a salmon-pink color of the water layer. The amount of mercaptan that reacted with the silver nitrate was calculated from the value obtained by subtracting the titration value of excess silver nitrate from that of the original quantity of silver nitrate added.

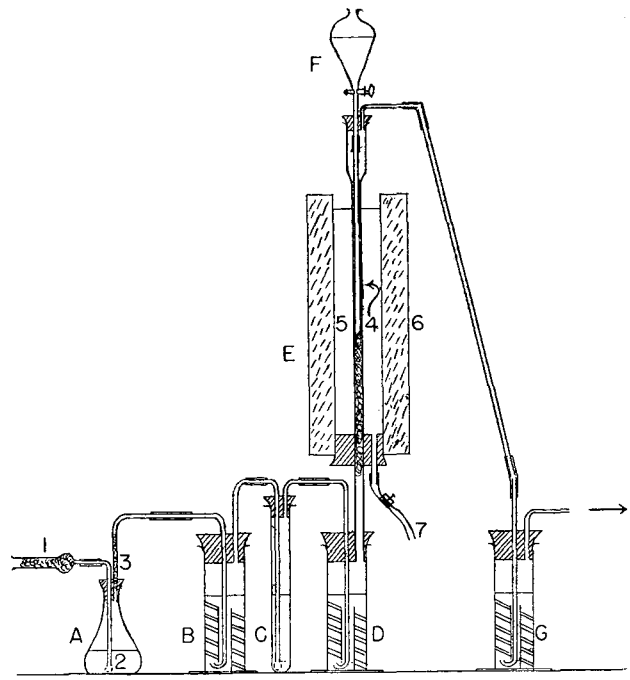


Figure 1. Apparatus for Trapping and Separating Volatile Organic Sulfur Compounds

A. 250-ml. Erlenmeyer culture flask with 100-ml. solution medium
1. Drying tube with cotton to free incoming air of microorganisms
2. Perforated bulb of aeration tube
3. Cotton to protect culture solution from air contamination

B. Gas-absorption bottle with mercuric cyanide for absorption of mercaptan

C. Test trap with mercuric cyanide

D. Gas-absorption bottle with benzene for absorption of dimethyl disulfide and dimethyl sulfide

E. Condenser cooled with iced water
4. Condenser tube filled with glass wool
5. Bath of iced water
6. Asbestos insulation
7. Waste line to drain condenser jacket, with screw clamp

F. 60-ml. separatory funnel for addition of benzene

G. Gas-absorption bottle with test trap of mercuric chloride

The reactions are as follows:

$$RSH + AgNO_3 = HNO_3 + RS\text{-}Ag\downarrow$$
$$AgNO_3 + NH_4SCN = NH_4NO_3 + AgSCN\downarrow$$

The red color develops with appearance of excess ammonium thiocyanate. A similar determination was made on the condenser trap solution of silver nitrate. The combined results provided the value for methyl mercaptan, from which the value for dimethyl disulfide was calculated.

A portion of the reduced and washed benzene solution was used to determine the melting point of the mercury salt of the methyl mercaptan derived from the dimethyl disulfide; the solution was treated with mercuric cyanide and the resulting precipitate was separated, purified, and tested in the same manner as the precipitate of mercuric dithiomethoxide derived from the methyl mercaptan in the absorbing solution of mercuric cyanide.

Determinations were made on 50-ml. aliquots for dimethyl sulfide. The aliquot was transferred to a 500-ml. separatory funnel

and 25 ml. of 10% silver nitrate acidified with nitric acid to below pH 2.0 were added to precipitate mercaptans formed by reduction of dimethyl disulfide. After being shaken vigorously, the water layer was drawn off and the benzene washed until the washings were neutral and free of silver. The benzene was filtered and transferred to a 500-ml. separatory flask containing 50 ml. of distilled water and an excess (10 ml.) of saturated bromine water (*10*). The mixture was shaken for 10 minutes, after which 10 ml. of 15% potassium iodide was added and the mixture was shaken again. Sodium thiosulfate (0.1*N*) was added to react with the iodine, and the solution was shaken and the water layer drawn off and recovered. The benzene was washed with three 50-ml. portions of water, and the washings were added to the original water solution. The total amount of solution was titrated with 0.1*N* potassium hydroxide, methyl red being used as indicator. The hydrobromic acid which was titrated is formed by the following reaction:

$$R_2S + Br_2 = R_2SBr_2 \xrightarrow{+\ H_2O} R_2SO + 2HBr$$

A portion of the benzene solution treated with silver nitrate to remove the mercaptan formed from the disulfide served as a source of material for melting point determinations representative of the mercury derivative of dimethyl sulfide. To obtain the material, the benzene was shaken with 3% mercuric chloride, filtered, washed, and recrystallized from hot benzene three times. The melting point as well as the mixed melting point with an authentic specimen of $2(CH_3)_2S.3HgCl_2$ was determined. This compound has a melting point of 158° C.

Scheme B. When dimethyl sulfide was present in the mixture of volatile products in the air stream, and when silver nitrate was used to react with the mercaptan formed from the dimethyl disulfide, low values for dimethyl sulfide were obtained according to Scheme A and the following procedure proved to be preferable. Bell and Agruss (*2*) did not report low values for this procedure. The starting material was the benzene in which the alkyl sulfide and disulfide were dissolved.

A 100-ml. portion of the benzene solution was reduced with powdered zinc and acetic acid as in Scheme A, and the benzene was washed and the benzene portion recovered as before. For the determination of dimethyl sulfide, a 50-ml. aliquot of the benzene was transferred to a 250-ml. separatory funnel and shaken with 25 ml. of alcoholic plumbite (*6*). The water fraction was removed, the benzene again treated with alcoholic plumbite, the water fraction removed, the benzene washed with water, and the benzene finally filtered and recovered. The dimethyl sulfide was determined on the benzene fraction by the bromine method described above.

If no dimethyl sulfide was found, a 50-ml. aliquot was treated with standard silver nitrate and titrated with standard ammonium thiocyanate according to the procedure for the reduced disulfide under Scheme A.

If dimethyl sulfide was found, dimethyl disulfide was determined as follows: To a 50-ml. aliquot of the benzene absorbent in a 250-ml. glass-stoppered Erlenmeyer flask were added 20 grams of pulverized mercurous nitrate (monohydrate) (*1*) and the mixture was shaken for 10 minutes. The solid, which removed the sulfide as $R_2S.x\ Hg(NO_3)_2$, was filtered off and washed with benzene, and the filtrate was added to the original benzene filtrate. The benzene was washed with three 50-ml. portions of distilled water in a separatory funnel, after which it was treated with powdered zinc and acetic acid to reduce the disulfide, and then treated with silver nitrate and titrated with ammonium thiocyanate according to the procedure for reduced disulfide under Scheme A.

EXPERIMENTAL

The procedures were tested on mixtures of known quantities of pure methyl mercaptan, dimethyl sulfide, and dimethyl disulfide. Because of flammability, toxicity, and volatility, special methods were used in sampling.

Rubber gloves were worn and all work was carried out in a hood in a well ventilated room. The tips of the glass-sealed bottles were broken off and samples of the liquids were withdrawn by 1-ml. syringes with long needles. The density of dimethyl sulfide is 0.8458 at 21° C. and that of dimethyl disulfide is 1.057 at 16° C. The liquids were brought to these temperatures by water baths before sampling. By reason of the low boiling point of methyl mercaptan (5.96° C.), its bottle was cooled in a bath of solid carbon dioxide, and the syringe used in sampling was cooled to below 0° C. There may have been some error in measuring the methyl mercaptan, for the density value of 0.896 at 0° C. was used. The liquids were added to 50 ml. of distilled water in a 250-ml. Erlenmeyer flask with the tip of the needle below the surface of the water. After the compounds were added, the flask was closed with a cork stopper covered and sealed with collodion. The flask occupied position *A* in Figure 1. To simulate the conditions of the tests with bacterial cultures, the air stream was drawn through the system for 3 days at a room temperature of approximately 28° C. Determinations were made in duplicate on solutions containing 0.1-ml. quantities of each of the three liquids. An untreated control solution was also tested.

The results of the determinations carried out according to Schemes A and B are summarized in Table I.

According to Scheme A, the values for dimethyl disulfide were somewhat too high and those for dimethyl sulfide were too low. This may have been due to reaction between dimethyl sulfide and silver nitrate used to determine and remove methyl mercaptan resulting from the reduction of dimethyl disulfide. The systematic analysis by Scheme B gave satisfactory results for these compounds. When only methyl mercaptan and dimethyl disulfide were present, Scheme A was preferable because the procedures were simpler. When dimethyl sulfide was also present, Scheme B gave more accurate results.

The results for methyl mercaptan were essentially the same in both schemes of analysis. Slow oxidation by air was found to convert between 2 and 3% of the methyl mercaptan to dimethyl disulfide under the conditions of the experiment, thus tending to give somewhat low values for methyl mercaptan and high values for dimethyl disulfide. The results of gravimetric and iodometric determinations of the mercuric precipitates of methyl mercaptan showed good agreement with those obtained by the titrimetric procedure, but they were somewhat low.

Most of the results were within 5% of the theoretical, which was adequate for the purposes for which the procedures were to be used. The degree of accuracy of the values seems to be

Table I. Determinations of Known Quantities of Methyl Mercaptan, Dimethyl Disulfide, and Dimethyl Sulfide

(In solutions containing 0.1.-ml. quantities of each compound)[a]

	Analytical Procedure					
	Titrimetric[b]		Gravimetric		Iodometric	
	S, mg.	% of theoretical	S, mg.	% of theoretical	S, mg.	% of theoretical
Methyl mercaptan (calculated S content of material used, 59.7 mg.)						
Scheme A	58.2	97.5	57.7	96.6	56.5	94.6
	57.4	96.1	57.1	95.6	56.0	93.8
Scheme B	56.8	95.1	56.7	95.0	56.2	94.1
	57.2	95.8	56.5	94.6	55.9	93.6
Dimethyl disulfide (calculated S content of material used, 72.0 mg.)						
Scheme A	74.4	103.3				
	73.4	101.9				
Scheme B	70.8	98.3				
	69.4	96.4				
Dimethyl sulfide (calculated S content of material used, 43.7 mg.)						
Scheme A	38.8	88.8				
	39.6	90.7				
Scheme B	41.9	95.9				
	42.3	96.8				

[a] Determinations on blanks of distilled water gave zero values in all cases.
[b] Results obtained by treatment of filtrate from the mercuric cyanide absorbent with mercuric nitrate and titration with ammonium thiocyanate.

very good, in view of the volatility of the compounds and the technical difficulties involved in sampling and in the analyses.

In no case did precipitate form in the trap solution of mercuric chloride (*G* in Figure 1), thus indicating that none of the mercaptan and sulfides failed to be absorbed by the mercuric cyanide and benzene.

Melting point determinations of the mercuric derivatives confirmed the identity of the methyl mercaptan, dimethyl disulfide, and dimethyl sulfide.

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Determination of Traces of Hydrogen Fluoride in Inert Gases

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A method has been developed for the determination of traces of hydrogen fluoride in inert gas sweepings. The gases are passed through a dilute solution of boric acid and the increase in conductivity of the solution, which is produced by the reaction between boric acid and hydrogen fluoride to form a complex strong acid, is measured. The relationship between conductivity and concentration of hydrogen fluoride was linear for the range 0 to 1 mg. of hydrogen fluoride. As little as 10 micrograms of hydrogen fluoride can be determined by this procedure. The method is particularly valuable for industrial application when no other ionizable gases are present.

THE detection and determination of traces of hydrogen fluoride in inert gases have been of recent interest. The ideal method for this type of determination is one that could be conducted at the site of the gas outlet, be relatively simple to accomplish, provide a rapid and accurate analysis, and be sufficiently sensitive to determine the gas in concentrations of the order of a few parts per million. Such limitations tend to eliminate the known colorimetric methods for fluoride. A proposed method which would meet these criteria is a conductometric measurement of a scrubbing solution through which the gases have been passed. Possible solutions which would serve as scrubbers include solutions which contain cations that form slightly soluble fluoride salts such as calcium, barium, and lead, or solutions which contain an ion that forms complexes with the fluoride ion. Water itself, because of the great solubility of hydrogen fluoride in water, could be used as a scrubber.

Boric acid, H_3BO_3, was considered a promising scrubbing solution in this instance. A solution of boric acid has several inherent advantages with respect to ultimate conductometric determination; it is slightly ionized in water ($K = 6.4 \times 10^{-10}$ at 25° C.) (*1*) and would hence have a specific conductance of the same order as water, and it reacts rapidly with fluoride ion to form a soluble complex acid. The reaction can be written:

$$H_3BO_3 + 3HF \longrightarrow HBF_3OH + 2H_2O \qquad (1)$$

Wamser (*4*) reports that monohydroxyfluoboric acid in aqueous solution is a strong acid (of the same order as hydrochloric acid), infinitely stronger than either boric acid of hydrofluoric acid ($K_1 = 6.89 \times 10^{-4}$ at 25° C.) (*2*). Hence, a solution of boric acid will show a distinct increase in conductivity when hydrogen fluoride is added. A study was made to adapt this reaction to the determination of traces of hydrogen fluoride in inert gas sweepings.

EXPERIMENTAL

A standard, dilute solution of hydrofluoric acid was used to provide hydrogen fluoride. A stock solution was prepared by diluting 1 ml. of 48% hydrofluoric acid to 1000 ml. and stored in a polyethylene bottle. This solution was standardized by a conductometric titration against standard alkali solution. Known amounts of hydrogen fluoride were taken from this stock solution by appropriate dilution. The scrubbing solutions were prepared from a stock solution of boric acid which contained 10 grams of boric acid, C.P. reagent grade, dissolved in 1 liter of freshly boiled, distilled water. This solution was not standardized, but its concentration calculated to give 0.016*M* boric acid. The experiments were conducted by adding from a buret known amounts of hydrofluoric acid to 100 ml. of boric acid and measuring the conductivity of the solution after each addition. The final volume of solution in all cases was 110 ml. Conductivity measurements were made with a Leeds and Northrup conductivity bridge using a "dip-type" cell with a cell constant of 0.1 cm^{-1}. Five concentrations of scrubbing solutions were used: 0.16*M*, 0.10*M*, 0.01*M*, 0.0016*M*, and 0.0003*M*. No precautions were taken to regulate the temperature. The temperature control of the conductivity bridge was set at the temperature of the dip cell.

Inert gases, which were suspected to contain hydrogen fluoride, were sampled by passing the gases through the scrubbing solution of boric acid and then through a wet-test meter to record its volume. For continuous monitoring of the gas stream, the conductivity cell was located directly in the gas outlet line; for periodic monitoring, the scrubbing solution was removed and its conductance measured. Borosilicate glass containers were used and showed no evidence of etching.

RESULTS AND DISCUSSION

A tabulation of the results is given in Table I, which shows that the conductivity of the boric acid scrubbing solution increases with the addition of hydrofluoric acid. As expected, the conductivity decreases with decreasing concentration of boric acid. A larger increase in conductivity is produced by the addition of 100γ of hydrofluoric acid to a solution of boric acid than

for 100γ added to water alone. It may be assumed that this increase is due to the formation of a stronger acid than either hydrofluoric or boric, thus producing the highly mobile hydrogen ion and increasing the conductivity of the solution. A comparison of the increases in specific conductance of the scrubbing solutions produced by the addition of hydrofluoric acid with the concentration of boric acid in the solution is presented in Table II.

The comparison indicates that a concentration range of 0.01*M* to 0.001*M* boric acid is optimum in order to obtain the maximum increase in conductivity per 100γ of hydrogen fluoride. No significant maximum between these concentrations was noted in subsequent experiments.

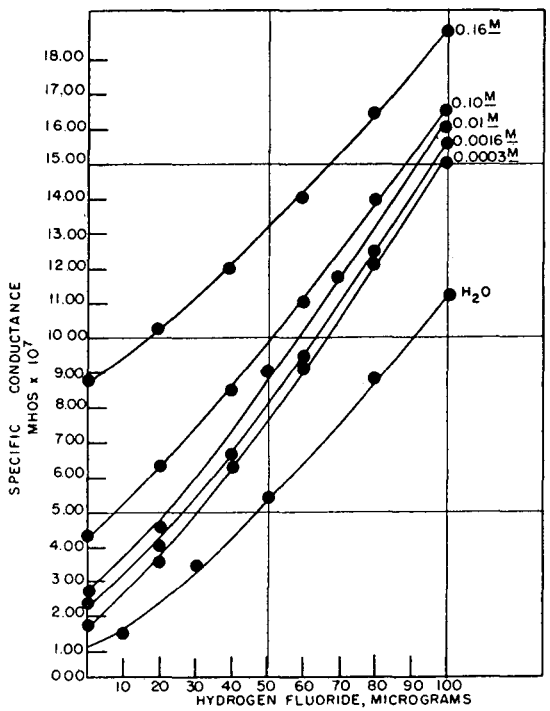


Figure 1. Effect of Micrograms of Hydrogen Fluoride on Conductivity of 100 Ml. of Boric Acid Solution

Table I. Specific Conductivity of Solutions of Boric Acid Containing Traces of Hydrofluoric Acid

Hydrogen Fluoride, γ	Mhos × 10⁷, Volume, 100 Ml. 0.16 *M*	0.10 *M*	0.01 *M*	0.0016 *M*	0.0003 *M*	0.0 (Water)
0	8.86	4.32	2.60	2.45	1.75	1.02
10	9.50	5.35	3.36	3.09	2.54	1.55
20	10.3	6.25	4.55	4.05	3.60	2.40
30	11.1	7.33	6.00	5.27	4.85	3.45
40	12.0	8.50	7.50	6.63	6.25	4.45
50	13.1	9.65	9.00	8.05	7.65	5.55
60	14.0	11.0	10.4	9.45	9.05	6.65
70	15.1	12.5	11.8	11.0	10.6	7.85
80	16.5	14.0	13.3	12.5	12.1	8.94
90	17.5	15.0	15.0	14.0	13.6	10.1
100	18.8	16.5	16.0	15.5	15.0	11.3

Table II. Increase in Specific Conductance of Solutions of Boric Acid by Addition of 100γ of Hydrofluoric Acid

Solution, Molarity	Conductivity, Mhos × 10⁷
0	10.3
0.0003	13.2
0.0016	13.0
0.003	13.3
0.015	13.4
0.10	12.2
0.16	10.0

The data from Table I have been plotted in Figure 1. This plot of conductance against micrograms of hydrogen fluoride added shows graphically the relationships mentioned previously. The slope is essentially a straight line for the optimum boric acid concentration range noted. The recommended procedure is to establish a standard curve for a determined boric acid concentration by adding hydrofluoric acid and measuring the conductivity. These measurements plotted as shown in Figure 1 serve as a standard curve. The slope is also a measure of the order of sensitivity of the method. With a standard volume of 100 ml. of scrubbing solution, the concentration of hydrogen fluoride in the solution is approximately 1×10^{-5} *M* following the addition of 100γ of hydrogen fluoride. The limit of sensitivity compares favorably with the most sensitive known colorimetric methods for fluorine. In actual practice it is more generally advantageous to express the value in terms of hydrogen fluoride per million parts of sweep gas. The use of a fairly sensitive conductivity bridge permits the measurement of as little as 1×10^{-6} *M* acid or 0.1γ per ml. (part per million). The reproducibility of the measurement of the specific conductivity of 0.01 *M* boric acid was of the order of 10% between lots. For solutions containing enough hydrogen fluoride to produce a specific conductance of the order of 1.0×10^{-6} mho, the precision of the measurements was approximately 8%. The error of the method is ±10γ for the range tested, 20 to 1000γ.

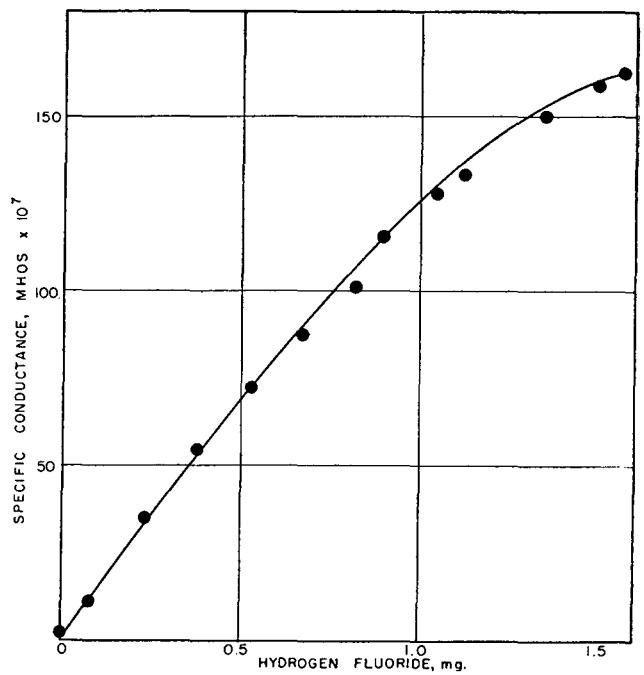


Figure 2. Effect of Milligrams of Hydrogen Fluoride on Conductivity of 100 Ml. of 0.01*M* Boric Acid Solution

Further experiments were conducted using 0.01*M* boric acid to determine the extent of linearity of the slope with increasing hydrogen fluoride concentration (Figure 2). The relationship appears to be linear up to 500γ of hydrogen fluoride. Beyond this concentration, the increase in conductivity per standard addition of hydrogen fluoride becomes smaller with increasing concentration of hydrogen fluoride. With a total of 1000γ of hydrogen fluoride present, the increase in conductivity per 100γ of fluoride is 5.0×10^{-7} mho, a factor of about 2 less sensitive than at the 100γ level.

The obvious limitation to the method is that the only ionizable species which are formed in the boric acid solution occur as a result of a reaction with hydrogen fluoride. This is not a serious

limitation for this particular application. The possibility exists that the conductometric measurement can be extended to the determination of traces of fluoride which can be liberated as aqueous hydrofluoric acid, as in the familiar pyrohydrolysis (*5*) technique.

The actual ionic species in the boric acid–hydrogen fluoride solutions were not identified. However, Wamser (*3, 4*) has studied the system boron fluoride–water and has established that the rate of Reaction 1 is extremely rapid. He has shown further that hydrolysis of monohydroxyfluoroboric acid proceeds rapidly as

$$HBF_3OH + H_2O \xrightarrow{\text{Rapid}} HBF_2(OH)_2 + HF \quad (2)$$

and

$$HBF_2(OH)_2 + H_2O \xrightarrow{\text{Rapid}} HBF(OH)_3 + HF \quad (3)$$

The reaction between hydrofluoric acid and monohydroxyfluoboric acid is extremely slow, however.

$$HBF_3OH + HF \longrightarrow HBF_4 + H_2O \quad (4)$$

The results of this investigation substantiate the work of Wamser. The increase in conductivity of the boric acid solution upon the addition of hydrogen fluoride was noted immediately. The readings were reproducible for at least 30 minutes for hydrogen fluoride concentration less than 1×10^{-4} M, but conductances of solutions of greater concentrations were not nearly as stable. The extreme is illustrated by the conductance of a solution of boric acid, 0.5 M with respect to hydrogen fluoride, the conductance of which was reproducible for only about 1 minute before a slow drift to higher readings became evident. The effect of the hydrolysis of a very dilute concentration of monohydroxyfluoroboric acid on its conductance is apparently insignificant, in which case readings are reproducible. As the concentration increases, however, this effect becomes increasingly pronounced and erratic readings are obtained.

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Titration Curve for Argentometric Determination of Cyanide

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The shape of the curve of p[Ag^+] in the titration of potassium cyanide with silver nitrate has been investigated, to determine the position of the inflection point relative to the equivalent point. The relations considered include the precipitation of silver cyanide and the effect of ammonia upon the titration. Equations are derived for the calculation of the equilibrium constants from the characteristics of the titration curve.

IN AN earlier article (*2*) on the interrelations of the equilibrium constants in aqueous solutions saturated with silver cyanide, the relation of the point of precipitation of silver cyanide or of silver iodide, as titration end point, to the equivalent point in the argentometric titration of cyanide was considered. The present article is concerned with the shape of the titration curve, or the curve of p[Ag^+] against the quantity of silver nitrate added, in order to determine the position of the inflection point in the curve and its relation both to the equivalent point and to the point of first appearance of a precipitate. Two sets of conditions are considered: the titration of pure aqueous potassium cyanide with silver nitrate, in which the hydrogen ion concentration is variable during the titration; and the titration of potassium cyanide in presence of excess of ammonia, during which the value of [H^+] is practically constant, fixed mainly by the ammonia.

A few of the expressions involved are identical with those of the previous discussion; two errors that crept into that paper as published are corrected here. For ease of comparison, all symbols remain as before, with the exception of the use, here, of A in place of K_a for the ionization constant of hydrocyanic acid.

NOMENCLATURE

c = analytical concentration of potassium cyanide
c_1 = analytical concentration of silver nitrate
b = analytical concentration of ammonia
c_3 = analytical concentration of potassium iodide
x = [Ag^+]
y = [$Ag(CN)_2^-$]
z = [$Ag(NH_3)_2^+$]
H = [H^+]
W = [H^+][OH^-] = 10^{-14}
A = [H^+][CN^-]/[HCN] = 4.0×10^{-10}
K_b = [NH_4^+][OH^-]/[NH_3] = 1.8×10^{-5}
K = [Ag^+][CN^-]^2/[$Ag(CN)_2^-$] = 1.4×10^{-20}
K' = [Ag^+][NH_3]^2/[$Ag(NH_3)_2^+$] = 6.0×10^{-8}
P = [Ag^+][CN^-] at saturation with AgCN, = 1.2×10^{-16}
P' = xy at saturation with AgCN, = $P^2/K = 1.03 \times 10^{-12}$
P_3 = [Ag^+][I^-] at saturation with AgI, = 8.5×10^{-17}
n = $c_1/(c/2)$
m = c_1/c
px = $-\log_{10} x = -\log_{10}[Ag^+]$
ϕ = $-dn/dpx$
ϕ = $-dm/dpx$
r = $1 + H/A$
Q = $P' + rP$
s = $1 + K_b/[OH^-]$
q = b^2/s^2K'
u = $\sqrt{cK/2x}$
v = $\sqrt{uW/A}$
$(\ )_e$ = value at equivalent point
$(\ )_i$ = value at inflection point
$(\ )_p$ = value required for precipitation
γ = activity coefficient of a univalent ion.
μ = ionic strength

The italic capitals represent mass constants, and activity constants are in bold face. The equality sign (=) is used only for relations which are exact by definition, and the symbol $\cong$ is used for all approximations, even if very accurate.

c and c_1 represent not initial concentrations or concentrations

of separate solutions, but the actual analytical concentration of potassium cyanide and silver nitrate, respectively, during the titration. The volume, however, is assumed to remain constant during the titration, so that c is treated as a constant throughout while c_1 is a variable, with $c_1 = n(c/2) = mc$.

The ratio n is significant in the usual titration, that to the equivalent point $c_1 = c/2$ or $n = 1$, in which the end point may be taken as an inflection point in the curve of px against n or as the appearance of a precipitate of either silver cyanide or silver iodide. The ratio m is used in connection with the continued precipitation of silver cyanide, starting near $n = 1$(or $m = {}^1/_2$), and carried to the equivalent point $c_1 = c$ or $m = 1$.

TITRATION OF PURE AQUEOUS POTASSIUM CYANIDE WITH SILVER NITRATE

Relations without Precipitation of Silver Cyanide. From the definitions, we have

$$c = 2y + [CN^-] + [HCN] = 2y + r\,[CN^-] \quad (1)$$

$$c_1 = x + y = c/2 + x - (r/2)[CN^-] \quad (2)$$

$$n = c_1/(c/2) = 1 + 2x/c - (r/c)[CN^-] \quad (3)$$

$$[CN^-]^2 = \frac{yK}{x} = \frac{(c_1 - x)K}{x} = \frac{(nc/2 - x)K}{x} \quad (4)$$

Also, the condition of electroneutrality means that $H - W/H = -[CN^-]H/A$; whence

$$H = \sqrt{AW/(A + [CN^-])} \quad (5)$$

Titration Curve before Equivalent Point, or with $n < 1$. With $y \gg x$ and hence $y \cong c_1$ or $nc/2$, Equations 1 and 4 give

$$x \cong \frac{nKr^2}{2c(1-n)^2} = \frac{nK}{2c(1-n)^2}\left(1 + \frac{H}{A}\right)^2 \quad (6)$$

H, however, is smaller than A until near the equivalent point. For pure potassium cyanide the value of H at the start is approximately $\sqrt{WA/c}$, and it remains, during the titration, always smaller than $\sqrt{W}$. This means that r ranges from $1 + \sqrt{W/cA}$, or about 1, to a maximum of less than $1 + \sqrt{W/A}$, or about 250. The combination of the definitions, moreover, gives

$$2c_1 = c + \frac{cH^4K}{A^2(W - H^2)^2} - \frac{H^2K(H + A)}{A^2(W - H^2)} - \frac{(H + A)(W - H^2)}{H^2} \quad (7)$$

so that $H = A$, and $r = 2$, when $c_1 \cong c/2 - W/A$. For c_1 appreciably smaller than $c/2$, therefore, we have $H < A$; and a rough expression for H is sufficient in the expression for r, or the parenthesis of Equation 6. For this purpose, with $r \cong 1$ and $y \cong c_1$, we may take $[CN^-] \cong c - 2y \cong c(1 - n)$ from Equation 1, so that Equation 5 becomes $H \cong \sqrt{AW/c(1-n)}$. This approximate value for H in this region of the titration corresponds to the effect of potassium cyanide as a base at the concentration $c(1 - n)$ and with ionization constant W/A. Equation 6 then becomes

$$x \cong \frac{nK}{2c(1-n)^2}\left[1 + \sqrt{\frac{W}{cA(1-n)}}\right]^2 \quad (8)$$

For the shape of the titration curve of px against n in this region, we first define, as a "buffer capacity," or as the reciprocal of the slope of the titration curve,

$$\phi = -dn/dpx = (\log_e 10)\,x(dn/dx) \quad (9)$$

Equation (6) then gives

$$\frac{1}{\phi} \cong \frac{1}{(2.3)}\left[\frac{1+n}{n(1-n)} + \frac{cH^3}{AW(H + A)}\right] \quad (10)$$

With the relatively small second term neglected, differentiation of Equation 10 shows that there will be a horizontal type of inflection point in the curve, corresponding to a maximum of ϕ, at

$$n \cong (\sqrt{2} - 1), \text{ or } 1/(\sqrt{2} + 1) \quad (11)$$

with $x \cong K(\sqrt{2} + 1)/4c$.

Titration Curve through Equivalent Point, or for $n \cong 1$. Even up to and just through the equivalent point, $[CN^-]$ remains greater than A. At $n = 1$, we have $[CN^-] = 2x/r$ from Equation 3, and $[CN^-]^2 \cong cK/2x$ from Equation 4, so that $8x_e^3 \cong cr_e^2K$. But H remains always smaller than $\sqrt{W}$, so that even with $r_e \cong \sqrt{W}/A$ in x_e, the value of $[CN^-]_e$, or $\sqrt{cK/2x_e}$, remains much greater than A, even down to $c = 10^{-3}$. From the start to just through the equivalent point, therefore, Equation 5 becomes $H \cong \sqrt{AW/[CN^-]}$, while at the same time $y \cong c_1$ or $nc/2$. Hence

$$H \cong \sqrt{AW\sqrt{2x/ncK}} \quad (12)$$

so that Equation 3 becomes

$$n \cong 1 + \frac{2x}{c} - \sqrt{\frac{nK}{2cx}} - \sqrt{\frac{W}{cA}}\sqrt{\frac{nK}{2cx}} \quad (13)$$

Both of these expressions hold from the very start of the titration to $n \cong 1$.

Near the equivalent point, then, when $nK/2cx \cong K/2cx$, Equation 13 becomes

$$n \cong 1 + \frac{2x}{c} - \frac{u}{c} - \frac{v}{c} \quad (14)$$

in which $u = \sqrt{cK/2x}$ and $v = \sqrt{uW/A}$. When $(1 - n)$ is still positive, but small, the neglect of the term $2x/c$ in Equation 14 gives, as a quadratic in $x^{1/4}$,

$$x^{1/2}c(1-n) - x^{1/4}\sqrt{\frac{W}{A}}\sqrt{\frac{cK}{2}} - \sqrt{\frac{cK}{2}} \cong 0 \quad (15)$$

At $n = 1$, Equation 14 gives, for the equivalent point,

$$x_e \cong \frac{1}{2}\sqrt[5]{\frac{cKW^2}{A^2}(1 + v)^4} \quad (16)$$

Since v is small compared to 1, the first approximation value of x_e may be used for x in v, to obtain

$$x_e \cong \frac{1}{2}\sqrt[5]{\frac{cKW^2}{A^2}\left(1 + \sqrt[5]{\frac{cKA^3}{W^3}}\right)^4} \cong \frac{1}{2}\sqrt[5]{\frac{cKW^2}{A^2}} \quad (17)$$

From Equation 12, then with $n = 1$, $H_e \cong \sqrt[5]{A^2W^3/cK}$. When $(1 - n)$ is negative, the neglect of the last two terms of Equation 14 gives

$$x \cong c(n - 1)/2 \quad (18)$$

This expression holds also for $n \gg 1$, if there is no precipitation of silver cyanide, for when $c_1 \gg c/2$, y then remains practically identical with $c/2$, and Equation 18 follows directly from Equation 2.

For the slope of the curve near and through the equivalent point, Equation 14 gives

$$\phi \cong 2.3\,(2x + u/2 + v/4)/c \quad (19)$$

$$d\phi/dpx \cong (2.3)^2(2x - u/4 - v/16)c \quad (20)$$

The "end-point" inflection or the vertical type of inflection corresponding to a maximum value of $|dpx/dn|$, therefore occurs at

$$x_i \cong \frac{1}{16}\sqrt[5]{\frac{cKW^2}{A^2}(1 + 4v)^4} \quad (21)$$

or as under Equations (16) and (17),

$$x_i \cong \frac{1}{16}\sqrt[5]{\frac{cKW^2}{2A^2}\left(1 + 8\sqrt[5]{\frac{cKA^3}{2W^3}}\right)^4} \cong \frac{1}{16}\sqrt[5]{\frac{cKW^2}{2A^2}} \quad (22)$$

Since $x_i < x_e$, from Equation 17, the inflection point occurs before the equivalent point; but the titration error, with the inflection point as end point, would be very small. [Actually, however,

precipitation of silver cyanide occurs even before the inflection point, as seen below, so that both x_i and x_e here represent metastable relations for the supersaturated solution.] Combination of Equations 14, 20, and 21 gives

$$n_i \cong 1 - \frac{30\,x_i}{c} + 3\sqrt{\frac{K}{2cx_i}} \cong 1 - \frac{15}{8}\sqrt[5]{\frac{KW^2}{2c^4A^2}} \qquad (23)$$

For the slope ϕ at the inflection point, Equations 19, 20, and 21 give

$$\phi_i \cong (2.3)\left(\frac{10\,x_i}{c} - \frac{1}{2}\sqrt{\frac{K}{2cx_i}}\right) \cong (2.3)\frac{5}{8}\sqrt[5]{\frac{KW^2}{2c^4A^2}} \qquad (24)$$

Relations Involving Precipitation of Silver Cyanide. During saturation with silver cyanide, we have $y = P'/x$, $[CN^-] = P/x$, and hence

$$H = \sqrt{AW/(A + P/x)} \qquad (25)$$

The first appearance of the precipitate, causing a break in the titration curve, occurs, under equilibrium conditions, when, from Equation 1, $x_p = (2\,P' + rP)/c$. Therefore the value of n at the first appearance of the precipitate is, from Equation 3,

$$n_p = 1 + \frac{2(2P' + rP)}{c^2} - \frac{rP}{(2P' + rP)} \qquad (26)$$

Practically, since r is always smaller than ~ 250, we have

$$x_p \cong 2P'/c \text{ or } 2P^2/cK \qquad (27)$$

and as long as $c \gg 2\,AP/K$, or $c \gg 7 \times 10^{-6}$, then, from Equation 25, $H_p \cong \sqrt{2\,APW/cK}$. With this expression for H in r in Equation 26 we see that n_p is less than 1 if $c^2 > 2(2\,P' + r\,P)^2/r\,P$, and hence for c greater than about 2×10^{-5}. At the same time, Equation 26 becomes

$$n_p \cong 1 - \frac{K}{2P}\left(1 + \sqrt{\frac{2PW}{cAK}}\right) \qquad (28)$$

fixing the titration error, if the first appearance of the precipitate (at equilibrium) is taken as the end point. (The negative sign in Equation 28 appears incorrectly as a positive sign in Equations 67 and 68 of *2*.)

For the titration curve during precipitation, in which the change of px is considered with respect to the ratio m (not n), the number of moles of precipitate formed per liter of solution is $c_1 - x - y = c - 2y - rP/x$, so that

$$m = c_1/c = 1 + x/c - Q/cx \qquad (29)$$

Here Q is defined as $Q = P' + rP = P' + P + HP/A$, with H as in Equation 25. At the equivalent point for the precipitation, then, or when $m = 1$, Equation 29 gives $x_e = \sqrt{Q} \cong \sqrt{P'}$ or $P/\sqrt{K}$.

Furthermore, since $dH/dx = H^3P/2x^2AW$, from Equation 25, the exact Equation 29 gives

$$\phi' = \frac{-dm}{dpx} = (2.3)\left(\frac{1}{c}\right)\left(x + \frac{Q}{x} - \frac{H^3P^2}{2x^2A^2W}\right) \qquad (30)$$

$$\frac{d\phi'}{dpx} = (2.3)\left(\frac{1}{c}\right)\left[x - \frac{Q}{x} + \frac{3H^3P^2}{2x^2A^2W}\left(1 - \frac{H^2P}{2xAW}\right)\right] \qquad (31)$$

The first two terms of Equation 31 are the largest, and since, near the equivalent point, $x \cong \sqrt{Q}$ and $H \cong \sqrt{W/(1 + \sqrt{K/A})} \cong 8.78 \times 10^{-8}$, the second term in the parenthesis amounts to ~ 0.114. The "end-point" inflection therefore occurs at

$$x_i \cong \sqrt{Q} - 3H^3K/4A^2W \cong \sqrt{Q} \qquad (32)$$

i.e., $x_i \cong \sqrt{P'}$ or $P/\sqrt{K}$. From Equation 29, then, $m_i \cong 1 - 3H^3K/2A^2W$, or $m_i \cong 1$, practically exactly.

With its third term neglected, Equation 30 gives $\phi' \cong (2.3)2x/c$, with x defined by Equation 29. At $m = 1$, or at the equivalent and inflection point, therefore,

$$\phi'_{e,i} \cong (2.3)\,2\sqrt{P'}/c, \text{ or } (2.3)\,2P/c\sqrt{K} \qquad (33)$$

Theoretical Titration Curves for Some Values of c. For the calculation of the curve without precipitation of silver cyanide, Equation 8 may be used to calculate x for specified n when $n < 1 - 2W/cA$; Equation 14 to calculate n for specified x when $n \cong 1$ (if n so calculated differs appreciably from 1, Equation 13 may be used for a second approximation); and Equation 18 when $n > 1$. For the curve during precipitation of silver cyanide, Equation 29, with H as in Equation 25, gives directly m for specified x; rearrangement of the equation may be used to calculate x for specified m:

$$x = -\frac{c(1-m)}{2} + \sqrt{\frac{c^2(1-m)^2}{4} + P' + P\left(1 + \sqrt{\frac{W/A}{A + P/x}}\right)} \qquad (34)$$

With $P' \gg P(1 + H/A)$, a first approximation value of x is easily used to see if a second approximation is needed. Prac-

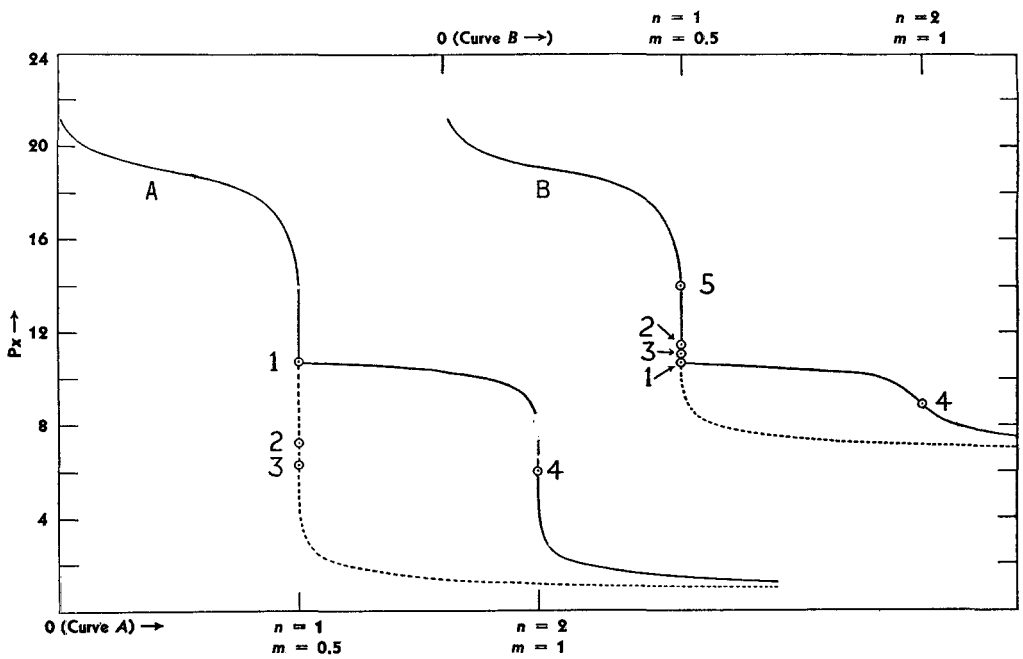


Figure 1. Titration of Aqueous Potassium Cyanide with Silver Nitrate for $c = 0.1$

A. Without NH_3
B. NH_3 at 0.2
1. Precipitation of AgCN
2. Inflection point
3. Equivalent point for $n = 1$
4. Equivalent point for $m = 1$
5. Precipitation of AgI, KI at 0.01

tically, Equation 34 means $x \cong P'/c(1 - m)$ for $m < 1$ and $x \cong c(m - 1)$ for $m > 1$.

The left half of Figure 1 shows the titration curve for pure potassium cyanide at $c = 0.1$. The solution is unsaturated up to point 1, where silver cyanide first begins to precipitate. The dotted section, 1-2-3, etc., represents supersaturated solution.

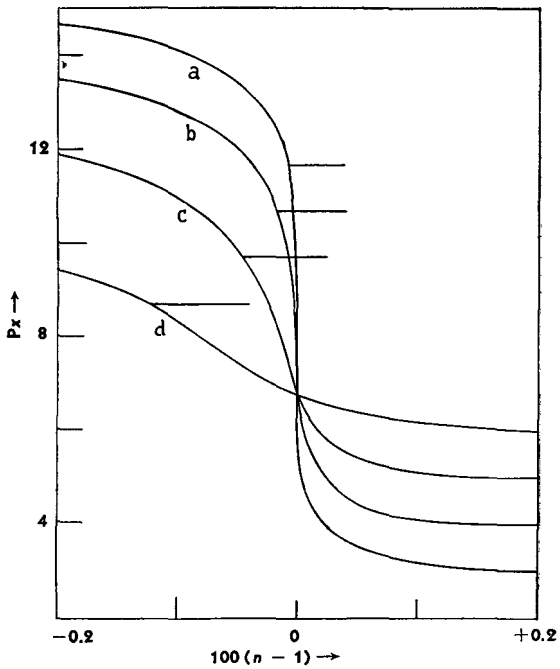


Figure 2. Titration Curves near $n = 1$, in Absence of Ammonia

a. $c = 1$
b. $c = 0.1$
c. $c = 0.01$
d. $c = 0.001$
Horizontal branch of each curve starts at point 1 of Figure 1, *A*, for precipitation of AgCN.

Point 2 is the inflection point, and 3 is the equivalent point at $n = 1$, both being metastable. Point 4 is the inflection and equivalent point for stoichiometric precipitation, at $m = 1$. The coordinates of points 1, 2, and 3 for various values of c are listed in Table I, in which "% error" $= 100\,(n - 1)$. The detailed course of the curves near $n = 1$ and near $m = 1$ is shown in Figures 2 and 3. These curves apply, strictly, for the addition of silver nitrate solution of such high concentration that the volume remains constant, so that c is a constant during the variation of ratio n or m. The approximate formulas for the relations near the equivalent points, however, hold regardless of the relatively negligible volume changes near these points, provided that c represents the final, not the initial, analytical concentration of the potassium cyanide.

With the inflection point taken as the end point, therefore, the error would be negative but practically negligible for the whole range of c considered. The precipitation of silver cyanide, however, would precede the inflection point which, in absence of ammonia, would occur only in the supersaturated solution. But even the precipitation of silver cyanide, if it should become visible when the solution first becomes theoretically saturated, would give only a negligible (negative) error as an end point.

Determination of Constants from px Curve. The two equilibrium constants in question are K, the instability constant of the complex ion $Ag(CN)_2^-$, and the solubility product of silver cyanide, which may be taken either as $P = [Ag^+][CN^-]$ or as $P' = P^2/K = [Ag^+][Ag(CN)_2^-]$.

The solubility product, P', may be obtained, theoretically, in

Table I. Titration of Pure Aqueous Potassium Cyanide with Silver Nitrate

[Values of px for precipitation of AgCN (point 1), at inflection point (point 2), and at equivalent point (point 3)]

c	Point	px	Percentage Error $100(n\text{-}1)$
1	1	11.686	-9.64×10^{-3}
	2	6.958	-2.54×10^{-4}
	3	6.093	0
10^{-1}	1	10.686	-1.79×10^{-2}
	2	7.195	-1.60×10^{-3}
	3	6.300	0
10^{-2}	1	9.686	-4.40×10^{-2}
	2	7.422	-1.00×10^{-2}
	3	6.504	0
10^{-3}	1	8.686	-1.26×10^{-1}
	2	7.642	-6.34×10^{-2}
	3	6.707	0

various ways: from x_p and c through Equation 27; from x at the end point of precipitation through Equation 32; and from the slope of the px curve and the value of c, at the end point of precipitation, through Equation 33. In each case, the thermodynamic constant is calculated from the mass constant so obtained, through the relation $\log \mathbf{P}' = \log P' + 2 \log \gamma$, while for the value of γ we have $2\mu \cong [K^+] + [NO_3^-] + y \cong c + c_1 + y \cong 2c$, since $y \cong c/2$ at $c_1 = c/2$ and $y \cong 0$ at $c_1 = c$.

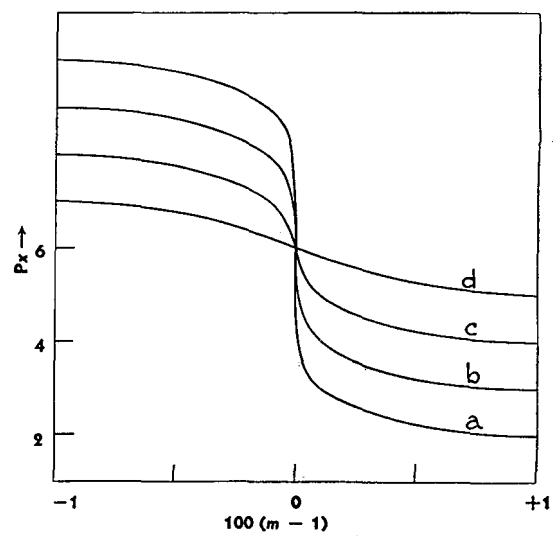


Figure 3. Titration Curves near $m = 1$, in Absence of Ammonia

a. $c = 1$
b. $c = 0.1$
c. $c = 0.01$
d. $c = 0.001$

The instability constant, K, may be obtained from corresponding values of x and n for given c, before precipitation, through Equation 13 as

$$K \cong \frac{2cx}{n}\left(-\sqrt{\frac{W}{4cA}} + \sqrt{\frac{W}{4cA} + 1 - n + \frac{2x}{c}}\right)^4 \qquad (35)$$

Roughly, for n appreciably smaller than 1, this becomes

$$K \cong 2cx\,(1 - n)^2/n \qquad (36)$$

as given directly by Equation 6 with $r \cong 1$. Again, $\log \mathbf{K} = \log K + 2 \log \gamma$, while $2\mu \cong [K^+] + [NO_3^-] + y + [CN^-] \cong c + 2c_1 + c(1 - n) = 2c$. K may also be calculated from the value of c and the slope of the px curve at the first appearance of the precipitate of silver cyanide, combined with the observed value of x_p, when Equation 19, with its first term neglected, gives

$$K \cong \frac{8x_p}{c}\left(-\sqrt{\frac{W}{32A}}+\sqrt{\frac{W}{32A}+\frac{c\phi}{2.3}}\right)^4 \quad (37)$$

If the value of P' is already known from the later portions of the curve, the theoretical value of $2P'/c$ may be used for x_p in this expression. In connection with Equation 37, moreover, $\mu \cong c$.

TITRATION IN PRESENCE OF AMMONIA

General Relations. For the relation between $[Ag(NH_3)_2^+]$ or z, and $[Ag^+]$ or x, we have, with b as the total or analytical concentration of ammonia,

$$b = [NH_3] + [NH_4^+] + 2z \quad (38)$$

so that

$$[NH_3] = (b - 2z)/s \quad (39)$$

in which s is defined as $1 + K_b/[OH^-]$. $[OH^-] \cong \sqrt{bK_b}$, so that with $b = 0.2$ (the recommended concentration for the Liebig-Dénigès titration, *1*), $s \cong 1.009$. Combining Equation 39 with the definition of K', we obtain

$$z = \frac{s^2K'}{8x} + \frac{b}{2} - \sqrt{\left(\frac{s^2K'}{8x}+\frac{b}{2}\right)^2 - \frac{b^2}{4}} \quad (40)$$

From this we see that as long as $x \ll s^2K'/4b$, or $x \ll 8 \times 10^{-3}$ if $b = 0.2$,

$$z \cong x(b^2/s^2K') \cong xq \quad (41)$$

In this titration, the significant considerations all involve very small values of x, so that, in general, z may be taken as xq and hence as much greater than x, since $q \cong 6.54 \times 10^5$ if $b = 0.2$.

For the value of H during the titration, the general relation is

$$H - W/H = -[NH_4^+] - [CN^-]H/A \quad (42)$$

With $H \ll [OH^-]$, since the solution is alkaline throughout, and with $[NH_4^+]$ from Equation 39, we have

$$[OH^-]^2 \cong bK_b\left(\frac{1 - 2z/b}{s}\right) + [CN^-]\frac{W}{A} \quad (43)$$

For $n < 1$, when $[CN^-] \cong c(1 - n)$,

$$[OH^-] \cong \sqrt{bK_b + c(1 - n)W/A} \quad (44)$$

This is the approximate formula for $[OH^-]$ in a solution containing two weak bases, ammonia at concentration b with ionization constant K_b, and potassium cyanide at concentration $c(1 - n)$ with ionization constant W/A.

When $n = 1$ or $n > 1$, $[CN^-]$ is very small, and it may be neglected in Equation 43, so that $[OH^-] \cong \sqrt{bK_b}$ and $s \cong 1 + \sqrt{K_b/b}$; hence

$$[OH^-] \cong \sqrt{bK_b}\left(\frac{1 - 2\,xq/b}{1 + \sqrt{K_b/b}}\right)^{1/2} \cong \sqrt{bK_b} \quad (45)$$

Titration Curve without Precipitation of Silver Cyanide. With

$$c_1 = x + z + y \cong z + y \cong xq + y \quad (46)$$

since $z \gg x$, we have, with Equation 1 for c,

$$n = c_1/(c/2) \cong 1 + 2\,xq/c - r[CN^-]/c \quad (47)$$

In the region $n < 1$, when the term $2\,xq/c$ is negligible and when $[CN^-] = \sqrt{yK/x} \cong \sqrt{ncK/2x}$, since $y \cong c_1$, the result is Equation 6 again, as in the absence of ammonia. Combination of Equations 6 and 44 then gives

$$x \cong \frac{nK}{2c(1-n)^2}\left[1 + \frac{W/A}{\sqrt{bK_b + c(1 - n)W/A}}\right]^2 \quad (48)$$

Differentiation of this expression leads to Equation 10, both with H as in Equation 44. Since the second term of Equation 10 is again negligible, we have the relations in Equation 11, the slope and position of the titration curve in this region being independent of the ammonia.

At the equivalent point, when $n = 1$ and $[CN^-] \cong \sqrt{cK/2x}$, Equation 47 gives

$$x_e \cong \frac{1}{2}\sqrt[3]{\frac{cKr^2}{q^2}} \cong \frac{1}{2}\sqrt[3]{\frac{cK(K')^2}{b^4}} \quad (49)$$

When $n > 1$, the last term of Equation 47 may be neglected, and the result is

$$x \cong c(n - 1)/2q \cong c(n - 1)K'/2b^2 \quad (50)$$

similar to Equation 18.

For a practical approximation of the inflection point near $n = 1$, H may be taken as a constant, according to Equation 45, since the term $2xq/b$ is very small compared to 1; accordingly, r, or $1 + H/A$, will also be taken as a constant ($r_b \cong 1.013$). Then with $[CN^-] \cong \sqrt{cK/2x}$, Equation 47 becomes

$$n \cong 1 + \frac{2xq}{c} = r_b\sqrt{\frac{K}{2cx}} \quad (51)$$

whence

$$\phi \cong (2.3)\left(\frac{2}{c}\right)\left(xq + \frac{r_b}{4}\sqrt{\frac{cK}{2x}}\right) \quad (52)$$

$$\frac{d\phi}{dpx} \cong (2.3)^2\left(\frac{2}{c}\right)\left(xq - \frac{r_b}{8}\sqrt{\frac{cK}{2x}}\right) \quad (53)$$

The inflection therefore occurs at

$$x_i \cong \frac{1}{4}\sqrt[3]{\frac{cr_b^2K}{2q^2}} \cong \frac{1}{4}\sqrt[3]{\frac{cK(K')^2}{2b^4}} \quad (54)$$

Then from Equations 51, 53, and 54,

$$n_i \cong 1 - \frac{6x_iq}{c} \cong 1 - \frac{3}{2}\sqrt[3]{\frac{b^2K}{2c^2K'}} \quad (55)$$

and from Equations 52, 53, and 54,

$$\phi_i \cong (2.3)\frac{6x_iq}{c} \cong (2.3)\frac{3}{2}\sqrt[3]{\frac{b^2K}{2c^2K'}} \quad (56)$$

Relations with Precipitation of Silver Cyanide. Since silver cyanide does not precipitate until $n \cong 1$, H is taken throughout as a constant, as long as $2\,xq/b \ll 1$ in Equation 45.

Again the precipitate appears when $x = (2P' + rP)/c$, or approximately at $x_p \cong 2P'/c$ as in Equation 27. In place of Equation 26, however, we now have, from Equation 47,

$$n_p \cong 1 + \frac{2q(2P' + r_bP)}{c^2} - \frac{r_bP}{(2P' + rP)} \quad (57)$$

Since $r_b \cong 1$, then $n_p > 1$ unless $c > 2bP'\sqrt{2/PK'}$, or unless c is greater than about 0.22 if $b = 0.2$. Approximately, Equation 57 means

$$n_p \cong 1 + \frac{4b^2P'}{c^2K'} - \frac{r_bP}{2P'} \quad (58)$$

With $c = 10^{-2}$, silver cyanide would not precipitate until $n \cong 1.027$, while for $c = 10^{-3}$, $n_p \cong 3.7$ (Equation 58 is a more correct approximation than Equation 124 of *2*.)

During the precipitation, the number of moles of precipitate formed per liter of solution is $c - 2y - rP/x = c_1 - x - y - z$, so that

$$m = c_1/c = 1 + (x + z - Q_b/x)/c \quad (59)$$

in which $z \cong xq$ and $Q_b = P' + r_bP \cong P'$. If $z \gg x$, and if q and Q_b are constants, then

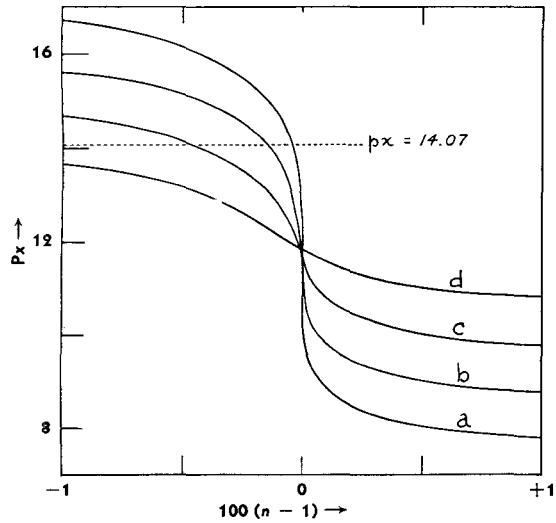


Figure 4. Titration Curves near $n = 1$, with Ammonia at 0.2

a. $c = 1$
b. $c = 0.1$
c. $c = 0.01$
d. $c = 0.001$
With KI at 0.01, AgI precipitates at $px = 14.07$.

$$\phi' \cong (2.3)(z + Q_b/x)/c \quad (60)$$

$$d\phi'/dpx \cong (2.3)^2(z - Q_b/x)/c \quad (61)$$

Thus so far as the assumptions involved in obtaining Equations 60 and 61 from Equation 59 are applicable, the inflection point occurs at the equivalent point, since x_e, from Equation 59 with $m = 1$, is identical with x_i, from Equation 61 with $d\phi/dpx = 0$. For the value of $x_{e,i}$ we may equate Q_b/x for z from these equations with the expression for z in Equation 40, obtaining

$$x_{e,i} \cong \sqrt{Q_b/q} + 2\,Q_b/b \quad (62)$$

From Equations 59, 61, and 62,

$$\phi'_{e,i} \cong (2.3)2x_iq/c \cong (2.3)(2b/c)\sqrt{P'/K'} \quad (63)$$

With decreasing c, the slope dpx/dm at this equivalent point is thus seen to become very shallow. All the relations of Equations 59 to 63, moreover, are meaningless for low c, since with $c < 2\sqrt{qP'}$, or $c < 1.6 \times 10^{-3}$ when $b = 0.2$, silver cyanide does not precipitate until $m > 1$; this is seen from Equation 58 with $n = 2$.

Precipitation of Silver Iodide. If potassium iodide is present at concentration c_3, then saturation with silver iodide occurs when $x_p = P_3/c_3$, and Equation 51 gives

$$n_p \cong 1 + \frac{2b^2P_3}{cc_3K'} - r_b\sqrt{\frac{c_3K}{2cP_3}} \quad (64)$$

For silver iodide to precipitate at the equivalent point, or at $n_p = 1$, the required value of c_3 would be P_3/x_e, with x_e as in Equation 49, or, directly from Equation 64, with $r_b \cong 1$, at $c_3 \cong 2bP_3\sqrt[3]{b/cK(K')^2}$. The required value, with $b = 0.2$, would then be:

c	c_3 Required
1	5.38×10^{-6}
0.1	1.16×10^{-5}
0.01	2.50×10^{-5}
0.001	5.38×10^{-5}

With larger c_3, $n_p < 1$, and the titration error is negative.

Some Titration Curves for Specific Values of c. For the titration curve without precipitation of silver cyanide, Equation 48 may be used to calculate x for specified n when $n < 1$; Equation 51 to calculate n for specified x near $n \cong 1$; and Equation 50 for $n > 1$. For the curve during precipitation of silver cyanide, Equation 59 may be used to calculate either m or x:

$$x \cong -\frac{c(1 - m)}{2q} + \sqrt{\frac{c^2(1 - m)^2}{4q^2} + \frac{P' + r_bP}{q}} \quad (65)$$

roughly, now, $x \cong P'/c(1 - m)$ for $m < 1$, and $x \cong c(m - 1)/q$ for $m > 1$.

The right half of Figure 1 shows the titration curve for potassium cyanide at $c = 0.1$ in presence of ammonia at $b = 0.2$. Point 1, for the first appearance of the precipitate of silver cyanide, now occurs below 3, the equivalent point, unless the concentration c is very large. Point 5 represents precipitation of silver iodide with $c_3 = 0.01$ (aproximately the value usually recommended, *1*). The coordinates of these points, for $b = 0.2$ and $c_3 = 0.01$, are listed in Table II for various values of c, and the course of the curves near $n = 1$ and near $m = 1$ is brought out in Figures 4 and 5.

Table II. Titration of Potassium Cyanide with Silver Nitrate in Presence of Ammonia

[At $b = 0.2$; values of px for precipitation of AgCN (point 1), at inflection point (point 2), at equivalent point (point 3), and for precipitation of AgI, with $[KI] = 10^{-2}$ (point 5)]

c	Point	px	Percentage Error, $100(n - 1)$
1	1	11.686	-5.63×10^{-3}
	2	11.193	-2.51×10^{-3}
	3	10.792	0
	5	14.07	-9.17×10^{-2}
10^{-1}	1	10.686	$+2.10 \times 10^{-2}$
	2	11.526	-1.16×10^{-2}
	3	11.127	0
	5	14.07	−0.290
10^{-2}	1	9.686	+2.69
	2	11.859	-5.39×10^{-2}
	3	11.460	0
	5	14.07	−0.917
10^{-3}	1	8.686	+269
	2	12.192	−0.250
	3	11.793	0
	5	14.07	−2.90

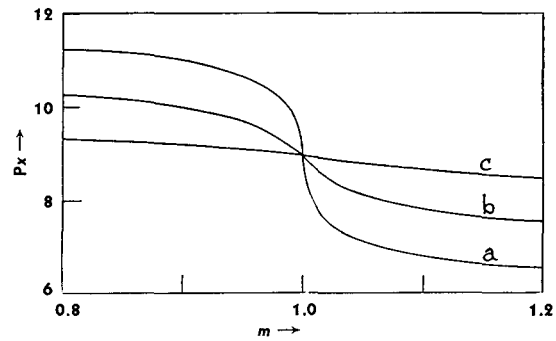


Figure 5. Titration Curves near $m = 1$, with Ammonia at 0.2

a. $c = 1$
b. $c = 0.1$
c. $c = 0.01$

For the values of the constants assumed, the precipitation of silver iodide as an end point would involve a considerable negative error, if potassium iodide is used at $c_3 = 10^{-2}$. The calculations would suggest that the inflection point, without potassium iodide, would be a much better end point in general. Because the silver iodide end point, even at $c_3 = 10^{-2}$, seems in practice to be satisfactory; however, it would again appear that something may be amiss with the numerical constants used (*2*).

Determination of Constants from px Curve. The solubility product, P', may be calculated as follows: from x_p and c, through the relation $x_p \cong 2P'/c$, as in the absence of ammonia; from x at the end point of precipitation, when $x \cong \sqrt{P'/q}$; from the slope of the px curve, and the value of c, at this point, through Equation 63.

The instability constant, K, may be obtained from corresponding values of x and n, for given c, before precipitation, through Equation 48; and since r, or the expression in the bracket of that equation, is hardly greater than 1, the approximate relation is merely Equation 36. K may also be derived from the slope of the titration curve, as at the inflection point near $n = 1$, through Equation 56, or at the point of first appearance of the precipitate of silver cyanide, through Equation 52, which becomes

$$K \cong \frac{8c}{x_p}\left[\frac{-\phi}{(2.3)r_b q}\right]^2 \qquad (66)$$

and in which x_p, if not actually measured, may be taken as $2P'/c$ if P' is known. The slope at the point of precipitation of silver iodide may also be used, when P_3/c_3 may be substituted for x_p in Equation 66.

The thermodynamic constants would follow from the mass constants as above, the ionic strengths being approximately the same both with and without ammonia.

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Determination of Dextran with Anthrone

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The anthrone method was used for the determination of concentration of dextran solutions. The effects of the factors involved in the method were studied and a procedure designed to improve the precision was evolved. Sources of error in the procedure were analyzed and it was concluded that the most probable source of error is variation in the blank. Nineteen different chemicals at different levels of concentration were tested for their effects on the analysis. The precision of the method was estimated by calculating standard deviations from 97 sets of duplicate blank determinations and 345 sets of duplicate sample determinations. The standard deviation for the samples, in absorbance units, is 0.0029, corresponding to 0.48% at an absorbance level of 0.600.

THE reaction obtained by heating carbohydrates with anthrone in sulfuric acid has been used in this laboratory to determine the concentration of dextran solutions. This reaction, first described as a qualitative test by Dreywood (*3*), has been converted by several investigators to a quantitative method. Most investigators have used the heat evolved by mixing the aqueous carbohydrate solution with the sulfuric acid solution of anthrone to furnish the heat required for the development of the blue-green color. With this technique, Morse (*10*) used the reaction to determine sucrose concentrations; Morris (*9*), for the determination of glucose, glycogen, and lactose; Viles and Silverman (*13*), for the analysis of starch and cellulose; Samsel and DeLap (*11*), for the determination of methylcellulose; and Bloom and Willcox (*2*), for the determination of dextran. This "heat of mixing" procedure has been investigated in this laboratory and found to be satisfactory if accuracy no better than ±5% is required.

For greater precision, it is necessary to keep the temperature rise, due to mixing the reagents, to a minimum and then place the reaction mixture in a controlled temperature bath for a specified time. Using this method, Siefter *et al.* (*12*) determined glycogen by heating a 1 to 2 mixture by volume of glycogen solution and 0.2% anthrone in 95% sulfuric acid for 10 minutes in a boiling water bath. McCready *et al.* (*8*) determined starch concentrations by the same procedure, but shortened the heating time to 7.5 minutes. For the determination of sodium carboxymethylcellulose, Black (*1*) dissolved the solid sample in 60% (by volume) sulfuric acid, added a 0.1% solution of anthrone in 60% (by volume) sulfuric acid, and heated the mixture for 15 minutes in a boiling water bath.

Among the workers who have controlled the heat supplied for the reaction, McCready *et al.* (*8*) published a time curve for 100° C., showing maximum absorption at 6250. A. at 7.5 minutes. This was substantiated by experimental work done at this laboratory. Although several authors have advised the use of fresh reagent, only Black (*1*) has published details of the effects of reagent age and acid concentration on the reaction, and his investigation was limited to cellulose and carboxymethyl cellulose. The authors investigated the influence of these factors on the analysis of dextran solutions and also studied the effects of temperature, anthrone concentration, and various impurities.

EXPERIMENTAL

It has been reported (*8, 9*) that the same absorption is developed from the reaction of anthrone reagent with equivalent amounts of glucose and starch or glycogen. It was assumed that the reaction with dextran would also be the same as with glucose, and National Bureau of Standards dextrose was used in the development of the method reported here. The validity of the assumption was established by work with purified dextran.

Selection of Wave Length for Absorption Measurements. Figure 1 shows the absorption curve for a 2 to 1 mixture (by volume) of 0.3% anthrone in concentrated sulfuric acid with 0.003% glucose solution heated at 100° C. for two periods of time. The

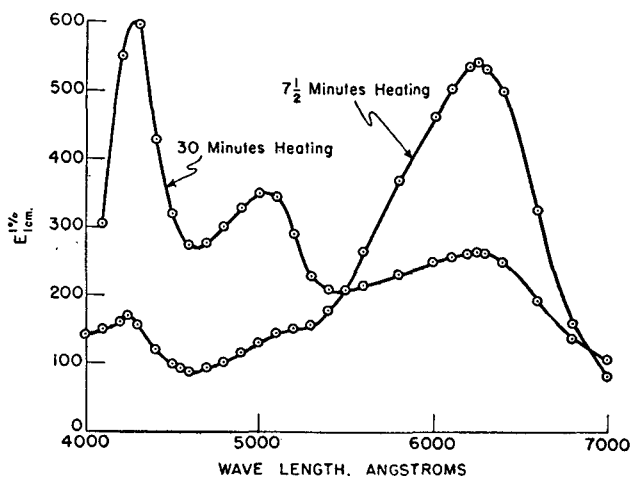


Figure 1. Effect of Heating Time on Anthrone-Glucose Absorption Curve

100° C., 75% acid

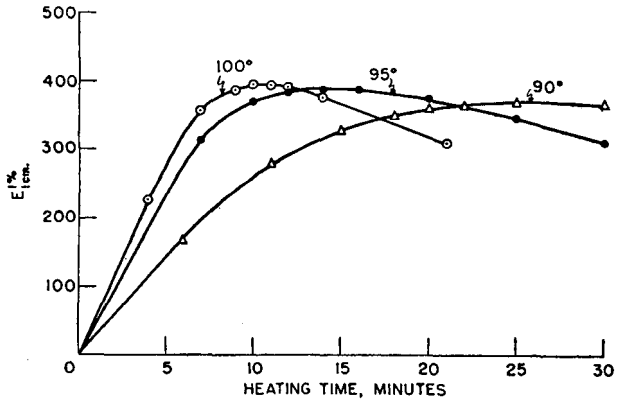


Figure 2. Effect of Temperature on Absorption at 6250 A. in 71.6% Sulfuric Acid

peak at 6250 A. was chosen for measurement, because the peaks at 5020 A. and at 4270 A. require a longer period of heating to develop.

Selection of Time, Temperature, and Acid Concentration for Reaction. Time curves were determined for temperatures from 80° to 100° C. at acid concentrations (in the reaction mixture) of 71.6, 75.4, and 79.6%. (All acid concentrations mentioned in this paper refer to weight per cent unless otherwise stated.) A study of Figures 2, 3, and 4 shows that with decreasing temperature the time curve flattens, the time required to reach maximum absorption increases and the value of maximum absorption decreases slightly. Decreasing acid concentration also flattens the curve and increases the time required to reach maximum absorption, but the value of the maximum absorption falls off rapidly. (The absorption coefficients shown in Figures 1 to 4 are based on a glucose concentration of 1 gram per 100 ml. of the reaction mixture.)

The factors considered in the selection of the temperature and acid concentration to be used for the reaction were the flatness of the time curve, the time required to reach maximum absorption, the ease of obtaining the chosen acid concentration, and the vapor pressure of the reaction mixture; 90° C. and 75% sulfuric acid (Figure 3) were chosen as a good compromise of the desired properties in the factors listed. There is little change in slope of the curve for a span of 4 minutes in the region of maximum absorption, and the time (16 minutes) required to reach maximum absorption is not excessive. The 75% acid concentration requires a simple 2 to 1 volume ratio of concentrated sulfuric acid to aqueous solution.

Anthrone Concentration in Reagent. Previous workers have used 0.05 to 0.2% anthrone in 95% sulfuric acid as the reagent for carbohydrate determination. Viles and Silverman (*13*), using the "heat of mixing" procedure, reported a maximum sensitivity at 0.16% anthrone with cellulose and starch standards. Data presented in Figure 5 show that for maximum precision under the conditions recommended in this paper the anthrone content of the reagent should be greater than 0.18 gram per 100 ml. of concentrated sulfuric acid.

Application of Beer's Law. Figure 6 shows that Beer's law applies to the absorption of reaction mixtures obtained from aqueous dextran solutions of concentrations less than 8 mg. per 100 ml. The departure from Beer's law was not due to insufficient anthrone, because doubling the anthrone concentration did not change the absorption coefficients at higher dextran concentrations.

Stability of Glucose and Dextran Solutions. Glucose solutions and, to a lesser extent, dextran solutions deteriorate unless protected from microbial contamination. It was found that solutions of either glucose or dextran would keep indefinitely at room temperature if 0.2 ml. of Roccal (10% alkyl dimethylbenzylammonium chloride, obtainable from the Winthrop Chemical Co., Inc.) or 2 mg. of phenyl mercuric acetate were added for each 100 ml. of solution. A 0.06% solution of glucose or dextran, preserved in this fashion, was diluted twentyfold for use as a standard for dextran determinations. The concentrations of the preservatives used in the diluted standard solutions did not interfere with the reaction with anthrone reagent.

Comparison of Glucose and Dextran in Reaction with Anthrone. Six aliquots of a glucose solution were run together with six aliquots of a dextran solution of equivalent concentration. At intervals, one each of the glucose and dextran solutions were removed simultaneously from the 90° C. bath, and cooled, and the absorbances were read. The resulting time curves, given by the data of Table IA, were identical within experimental error.

Another set of 11 glucose samples were run (16 minutes, 90° C., 75% sulfuric acid) simultaneously with a set of 12 samples of dextran solution of equivalent concentration (Table IB). The agreement of the average absorbances confirms the reports of other investigators that a polymeric carbohydrate behaves in the same way as its hydrolyzed solution in the reaction with anthrone.

APPARATUS. Spectrophotometer, Beckman Model DU
Test tubes, borosilicate glass, 25 × 200 mm.
Loose-fitting borosilicate glass test tube caps or small beakers
Bath, ethylene glycol, maintained at 90° C.
Bath, water, cooling
Wire basket, to hold several 25 × 200 mm. tubes
Pipet 10-ml., orifice enlarged and fiducial mark adjusted to deliver 10 ml. of concentrated sulfuric acid in 20 to 30 seconds

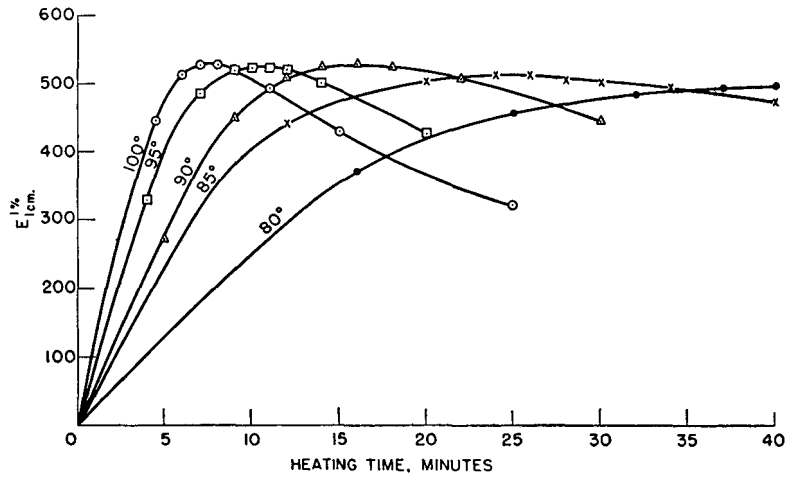


Figure 3. Effect of Temperature on Absorption at 6250 A. in 75.4% Sulfuric Acid

REAGENTS. Standard, pure dextran (if available) or NBS dextrose
Distilled water
Anthrone reagent, 2 grams of anthrone (*4*), dissolved in 1 liter of concentrated sulfuric acid (ACS reagent grade). Anthrone samples from several commercial sources were tested and found to vary widely as to stability in concentrated sulfuric acid.

Procedure. Place the wire basket containing the test tubes in a rapidly circulating cold water bath (10° to 15° C.). Using the pipet with enlarged orifice, deliver 10 ml. of anthrone reagent into each tube, allowing the same drainage time for each delivery. Cover tubes with loose-fitting caps.

Pipet 5 ml. of sample, diluted to a concentration of 2 to 4 mg. per 100 ml., into each tube, carefully forming a layer above the anthrone reagent. Include two blanks, using 5 ml. of distilled

Table I. Comparison of Glucose with Dextran in Reaction with Anthrone Reagent

Heating Time, Min.	Absorbance at 6250 A. (1-Cm. Cells) Glucose (3.00 mg./100 ml.)	Dextran (2.70 mg./100 ml.)
A. Variation of Absorbance with Time of Heating (90° C., 75% H_2SO_4)		
10	0.485	0.484
14	0.536	0.536
16	0.543[a]	0.548[a]
18	0.541	0.542
20	0.534	0.537
24	0.511	0.510
B. Samples Heated Simultaneously for 16 Minutes (90° C., 75% H_2SO_4)		
	0.581	0.572
	0.569	0.569
	0.569	0.573
	0.572	0.581
	0.570	0.568
	0.570	0.575
	0.573	0.575
	0.575	0.573
	0.574	0.575
	0.572	0.572
	0.571	0.573
		0.572
Mean	0.5724[a]	0.5732[a]
Standard deviation 0.0033 or 0.58%		

[a] Anthrone reagent used for A was several days old, while that of B was freshly prepared, which explains difference in absorbance at 16 minutes.

water instead of sample. Also include two glucose or dextran standards with each set of samples.

After the aqueous solutions have been added to all of the tubes, shake each tube vigorously, while keeping immersed in the cold water bath, until contents are thoroughly mixed and at about room temperature. Place the basket of tubes in the 90° C. bath for 16 minutes, then return them to the cold water bath until contents are cooled to room temperature.

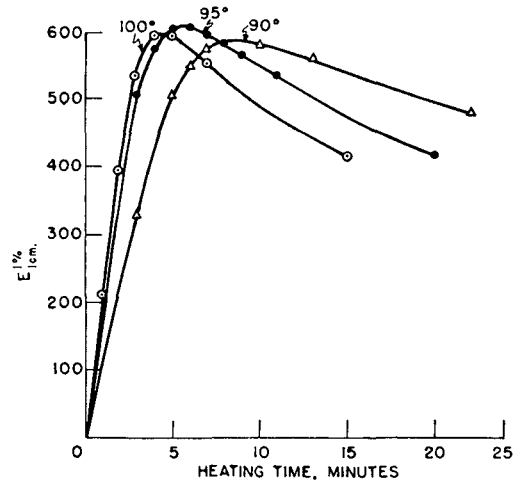


Figure 4. Effect of Temperature on Absorption at 6250 A. in 79.6% Sulfuric Acid

Read immediately the absorbances of the samples, standards, and blanks in 1-cm. absorption cells, using water as a reference. If the absorbances of the blanks disagree by more than 0.005, use the lower for the correction of sample and standard absorbances, as it is probable that the higher is due to carbohydrate contamination.

Calculation

$$C_x = \frac{C_{std}\,(D_x - D_b)}{D_{std} - D_b}$$

C_x = concentration of dextran sample. (If the original sample required dilution to bring it into the concentration range necessary for a determination, the C_x must be multiplied by the appropriate dilution factor.)

C_{std} = concentration of dextran standard (if a glucose standard is used, its concentration is multiplied by 0.900 to give its dextran equivalent.)

D_x = absorbance of sample

D_b = absorbance of blank

D_{std} = absorbance of standard

SOURCES OF ERRORS

Instability of Anthrone Reagent. The absorption coefficient at 6250 A. for dextran, reacted with 1-week-old anthrone reagent, is 5 to 10% lower than when freshly prepared anthrone reagent is used. This decrease in absorption is erratic and not strictly proportional to the age of the reagent, so that a standard solution of glucose or dextran must be run simultaneously with each group of samples. Figure 7 shows that Beer's law applies when 1-week-old reagent is used. Other investigators, using a 100° C. bath or the heat supplied by mixing, have noted inconsistent results with reagent less than 4 hours old, and McCready *et al.* (*8*) have indicated that the reagent should not be more than 2 days old. Using the method outlined in the present paper, reliable results were obtained using reagent ranging from 1 hour to 7 or 8 days old.

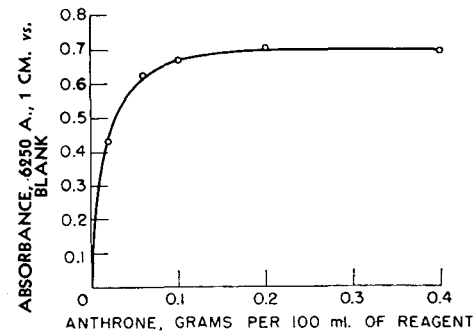


Figure 5. Effect of Anthrone Concentration on Absorbance of Anthrone-Dextran

16 minutes, 90° C., 75% acid

Loewus (*7*) has recommended a "heat of mixing" procedure which involves mixing 2 ml. of sample solution with 5 ml. of concentrated sulfuric acid and 0.5 ml. of a 2% solution of anthrone in ethyl acetate. The latter solution is said to be stable, which would eliminate the need for a standard solution with each set of samples. However, standardization would still be required for each bottle of sulfuric acid, in addition to the handling of a third solution for each determination. Accurate work would necessitate better control of heating time and bath temperature if a standard was not included with each set of samples.

Variation of Heating Time and Bath Temperature. The inclusion of a dextran solution of known concentration with each set of samples makes the analysis relatively insensitive to heating time and bath temperature, because each of these factors is constant for all samples in a particular set of determinations. It is, of course, necessary that the bath have good circulation, so that all tubes are heated evenly.

Variation of Acid Concentration of Anthrone Reagent. Because of the inclusion of a dextran solution of known concentration, the acid concentration of the reagent is not an important source of error. However, it is desirable that the time of heating fall on a point of the time curve (Figure 3) where the slope of the curve is small—i.e., near maximum absorption. Therefore, it is advisable to determine if the use of ACS reagent grade sulfuric acid of unadjusted concentration will change the time curve to the extent that the heating time would correspond to a point on the curve where absorption is changing rapidly with heating time. The concentration of most ACS reagent grade sulfuric acid is between 95 and 97%. When diluted with half its volume of

water, the concentration is decreased to 74.7 to 76.3%. Interpolation at these values in Figure 8 shows that the times required to reach maximum absorption are 17.4 and 14.2 minutes, respectively. Thus, the 16 minutes' heating used in the procedure would, in the worst case, be about 2 minutes past the time of maximum absorption. Examination of the curves (Figures 2, 3, and 4) shows that at this distance from the peak, the slope of the curve is still small. Thus, it is permissible to use ACS grade sulfuric acid as a solvent for anthrone without adjusting the concentration.

Variation in Rise of Temperature When Mixing Samples with Reagent. The method of mixing the aqueous solutions with the anthrone reagent should be standardized as much as possible to prevent any great variation in temperature increase. Experiment showed that when 10 ml. of concentrated sulfuric acid was added directly to 5 ml. of water in a tube not held in a cold water bath, the temperature of the contents rose to 130° C. When the water was layered upon the sulfuric acid and the contents were mixed in a cold water bath (15° C.), the temperature of the contents rose to 85° C. If each sample is mixed in a cold water bath for the same length of time, any variation in temperature should be negligible in comparison with the total of 16 minutes' heating at 90° C.

This is substantiated by an experiment in which 0.1 to 0.2 gram of a solution containing 0.1 gram of dextran per 100 ml. was weighed into each of six small glass cups. The solutions were then evaporated to dryness under an infrared lamp and the cups were dropped into test tubes containing a previously mixed and cooled mixture of 10 ml. of anthrone reagent and 5 ml. of water. The test tubes were thoroughly shaken to dissolve the dried dextran in the reagent, then heated 16 minutes at 90° C., and cooled, and the solutions read on the spectrophotometer. This procedure eliminated completely the heat of mixing, but a plot of absorbance *vs.* dextran content showed no better precision than was obtained by the usual method.

Variation in Delivery of Reagent. If slightly more than 10 ml. of anthrone reagent is added to 5 ml. of the dextran solution, the sulfuric acid concentration of the reaction mixture will be slightly increased, which causes an increase in the absorption at 6250 A. However, the additional reagent also increases the volume of the reaction mixture, so that the concentration of dextran is decreased. These two effects tend to counteract one another, so that the method is rather insensitive to the amount of reagent added. Figure 9 shows the effect on the absorbance of varying the volume of the anthrone reagent added to 5 ml. of standard dextran solution. Curves are shown for anthrone in 95, 96, and 97% sulfuric acid. With 96% sulfuric acid, a delivery error of ±1% causes no more than 0.1% error in the absorbance read. When the sulfuric acid concentration is either decreased or increased from 96%, the effect of an error in the measurement of the reagent is more pronounced. With 95 or 97% sulfuric acid reagent, about 0.3% error in absorption is caused by a 1% error in the delivery of the reagent. It was found that a 10-ml. pipet, with the orifice enlarged so that concentrated sulfuric acid empties in about 20 seconds, is satisfactory if about 10 seconds' extra drainage time is allowed. In 13 deliveries from such a pipet, the standard deviation from the mean was only 0.14%.

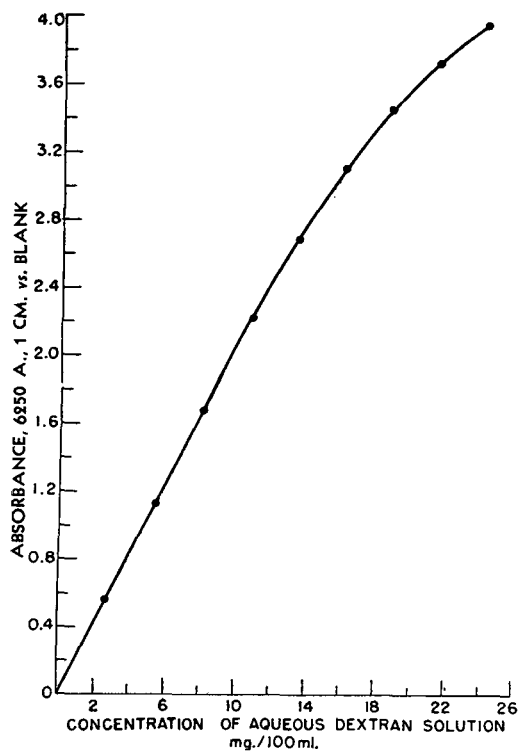


Figure 6. Absorbance as a Function of Dextran Concentration

16 minutes, 90° C., 75% acid

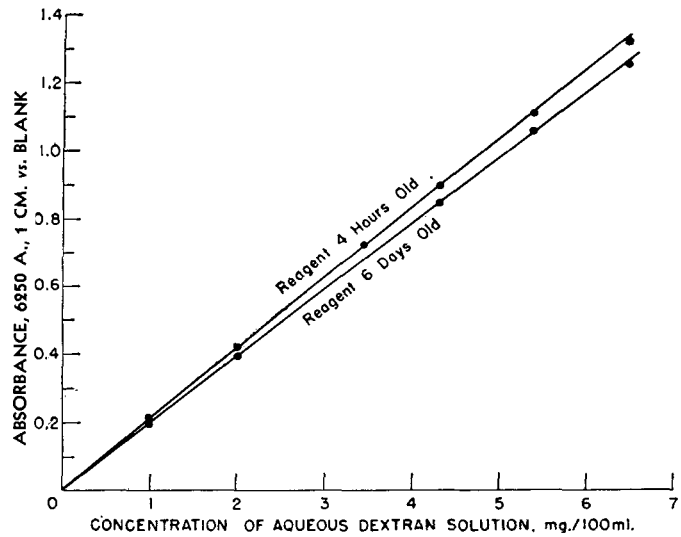


Figure 7. Effect of Age of Reagent on Relationship between Absorbance and Dextran Concentration

16 minutes, 90° C., 75% acid

Color Stability. Other workers (*11*, *12*) have reported that the absorption at 6250 A. of carbohydrate-anthrone solution remains constant for several hours. The present authors, using the procedure for dextran determinations outlined in this paper, have found the color stability to be variable. For some determinations, the absorption at 6250A. did not change for more than an hour after samples were removed from the 90° C. bath; on other occasions, a 1% decrease in absorption per hour was noted. For careful work, it is necessary to measure the absorption of samples immediately after the set has cooled to room temperature.

Evaporation Losses during Heating Period. The vapor pressure of 75% sulfuric acid at 90° C. is 20 mm. of mercury (*5*), comparable to the vapor pressure of water at room temperature. When the tubes containing the reaction mixture were weighed before and after heating 30 minutes at 90° C., a net loss of 6 mg. was found. Such a small loss would be negligible as a source of error.

Effect of Fructose and Other Impurities on Determination of Dextran. Fructose is the principal by-product of the action on sucrose of dextran-synthesizing bacteria or their isolated enzymes and commonly occurs, therefore, as an impurity in dextran fractions separated from the synthesis mixtures. The concentration

of fructose in dextran fractions may be determined by a reducing power method, provided that the dextran is of sufficient molecular weight to contribute relatively few reducing end groups to the reaction. It is then necessary to know the absorption developed by fructose with anthrone reagent in order to correct the anthrone determination of dextran for the absorption contributed by fructose. Koehler (*6*) reports that fructose heated at 100° C. with 0.2% anthrone reagent develops in 2 minutes a maximum absorption about 75% greater than that developed by glucose-anthrone in 10 minutes. With continued heating at 100° C., Koehler found that the fructose-anthrone absorption gradually faded, but was still greater after 10 minutes than that of glucose-anthrone heated for the same time. Investigation at this laboratory supported

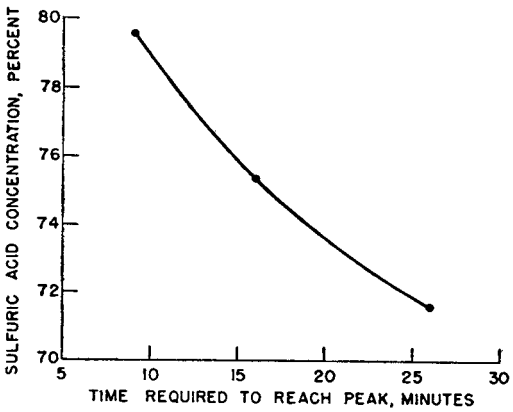


Figure 8. Effect of Sulfuric Acid Concentration on Time Required to Reach Maximum Absorption at 6250 A.

Koehler's evidence for the comparatively rapid reaction of fructose with anthrone. Fructose solution developed the characteristic green color when mixed with anthrone reagent in a cold water bath. The absorption curve of this fructose-anthrone solution (with no further heating) was identical in shape but 20% higher than that of a glucose-anthrone solution heated 16 minutes at 90° C. When the fructose-anthrone was heated 16 minutes, absorption at 6250 A. decreased to an average value of 94% of that of glucose-anthrone and this was used as the correction factor. A standard deviation of 2.7% was found for 12 determinations of the ratio of fructose absorption to that of glucose, the respective absorptions determined simultaneously for 16 minutes' heating at 90° C. Comparison with the standard deviation of 0.5% found for glucose-anthrone indicates the relative lack of reproducibility of the absorption of fructose-anthrone.

Table II shows the concentrations at which several possible contaminants interfere with the reaction. The effect of sodium chloride is important to those wishing to determine dextran in saline solutions. If the concentration of sodium chloride is more than twice that of dextran, results will be high. Apparently, the chloride ion is the interfering substance, as sodium sulfate does not interfere and hydrogen chloride affects results in about the same fashion as sodium chloride.

The concentrations at which preservatives for sugar solutions begin to interfere with the anthrone reaction should be noted. In order to avoid corrections, the concentration ratio of preservative to carbohydrate should not exceed 10 for Roccal or 4 for phenyl mercuric acetate. Preservation of sugar solutions by saturation with toluene is the practice in some laboratories. Table II shows that a carbohydrate solution, when diluted to the concentration range necessary for the determination, should not be more than 2% saturated with toluene.

Presence of Carbohydrate Impurity. This is believed to be the principal source of error in the method. Because the reaction mixture contains only 100 to 200 micrograms of dextran, the presence of as little as 1 to 2 micrograms of extraneous carbohydrate material will cause a 1% error. Any contamination of a solution with cellulose fiber from the atmosphere or from laboratory manipulations will cause high results in the determination by anthrone. It is imperative that glass apparatus and the reaction mixtures themselves be protected from contamination at all times.

Table II. Effect of Foreign Materials on Determination of Dextran with Anthrone

Substance	Concn., G./100 Ml. Dextran Solution[a]	Error, %
Acetic acid	1	−3.7
	0.3	−1.1
Acetone	2.5	−1.5
	1	<1
Acetophenone	5% saturated	<1
Benzaldehyde	20% saturated	+1.9
Benzene	20% saturated	−1.1
Benzoic acid	80% saturated	+3.4
	20% saturated	<1
Butanol	0.08	−9.1
	0.008	−1.5
Ethanol	3	+3.3
	1	<1
Formaldehyde	0.0001	−3.5
	0.00005	<1
Hydrogen chloride	0.36	+13.3
Methanol	3	+1.5
	1	<1
Methyl ethyl ketone	1	−12.7
	0.3	−1.9
	0.1	<1
Phenol	0.0006	−3
	0.0001	<1
Phenyl mercuric acetate	0.025	−2.5
	0.020	−1.0
Roccal	1	−5.2
	0.5	−4.0
	0.1	−1.6
	0.05	<1
Saliva	86 mg. (in reaction mixture)	+10
Sodium chloride	0.1	+9.5
	0.05	+6.0
	0.01	+1.2
	0.005	<1
Sodium sulfate	0.32	<1
Toluene	20% saturated	−8.0
	10% saturated	−2.2
	5% saturated	−1.2
	2% saturated	<1

[a] 3 mg. of dextran per 100 ml.

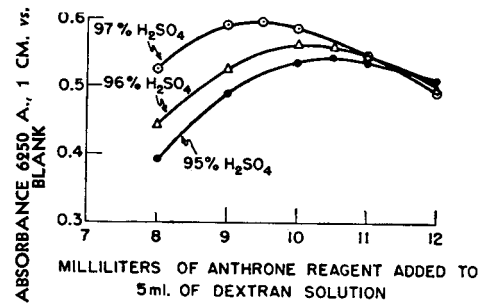


Figure 9. Effect on Absorbance of Variation in Volume of Anthrone Reagent

PRECISION OF THE METHOD

Since the absorption of the anthrone–sulfuric acid–dextran reaction varies according to the age of the anthrone reagent, it is impossible to compare one day's absorbance with another as a measure of the precision of the method. However, the standard deviation may be calculated from a large number of sets of duplicates (Table III).

For n sets of duplicate measurements,

$$\text{Standard deviation} = \sqrt{\frac{1}{2n}(\text{the sum of } d^2)}$$

where d is the difference between duplicates and is taken for each of the n pairs.

The duplicates referred to in Table III were in each case 5-ml. aliquots from the same final dilution of dextran solution, so that dilution errors are excluded from the calculation of the standard deviation.

Table III. Precision of Anthrone Method

	Absorbance at 6250 A. (1-Cm. Cell)	
	Blanks *vs.* water	Samples *vs.* water
No. of pairs of duplicates	97	345
Range of absorbance	0.001 to 0.037	0.320 to 0.888 (80% 0.500 to 0.700)
Range of difference between duplicates	0.000 to 0.014	0.000 to 0.015
Standard deviation	0.0024	0.0029

As the standard deviation of the blanks (0.0024) is more than 80% of the standard deviation of the samples, the major source of error must be due to the relatively poor reproducibility of the blank. Although a value of the blank absorption is determined and subtracted from the absorptions of the samples, the variability of the blank remains in the corrected sample absorptions. The most likely explanation of blank variability would seem to be contamination by minute quantities of extraneous carbohydrate.

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Determination of the Gamma Isomer Content of Benzene Hexachloride

By Chlorine-36 Isotope Dilution Method

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Considerable disagreement among a number of analytical methods for determination of the gamma isomer of benzene hexachloride led to the development of a new isotope dilution method using chlorine-36-labeled pure gamma isomer as a tracer. A known quantity of chemically pure radioactive gamma isomer of benzene hexachloride, labeled with chlorine-36, is added to a known weight of a technical benzene hexachloride sample of unknown gamma content. A sample of pure gamma isomer is then isolated from the mixture by an extraction procedure. The specific activity of the isolated material is compared to that of the original labeled isomer. The standard deviation of the method is ±0.2 % in gamma isomer content. Four determinations can be made by one analyst in an 8-hour day. This analytical procedure can be classified as an absolute method and is being used as a referee for other routine methods for the determination of the gamma isomer. It is being used to analyze benzene hexachloride samples having gamma contents ranging from 1 to 50%.

THE industry has been without an absolute analytical method for the determination of the gamma isomer content of technical grade benzene hexachloride. Infrared, polarographic, and chromatographic techniques have been used, but considerable disagreement has occurred at times when different laboratories have attempted to check each other. It was the purpose of the work described herein to develop an isotope dilution method of analysis which is absolute and precise.

A successful absolute method was developed which is practical and requires no special technique. Its standard deviation was found to be ±0.2% in gamma isomer content. The time required for a single analysis is about 4 hours. Four determinations can be made simultaneously in an 8-hour day.

[1] Deceased.

Trenner *et al.* (7) developed an isotope dilution method for the determination of the gamma isomer of benzene hexachloride using deuterium-labeled gamma isomer as a tracer. The method herein described is different in that a radioactive isomer has been used as the tracer.

Throughout the experimental procedure, the chemically pure labeled gamma benzene hexachloride is referred to as the labeled standard.

PREPARATION OF LABELED STANDARD

The initial step in an isotope dilution method of analysis is to prepare a chemically pure radioactive compound which is identical in structure to the compound to be determined. In the method described it was necessary to prepare a quantity of pure

gamma isomer of benzene hexachloride labeled with chlorine-36.

Radioactive Chlorination of Benzene. This procedure is based upon the known rapid establishment of exchange equilibrium between chlorine and chloride ion in aqueous solution. Inactive chlorine bubbled through radioactive hydrochloric acid becomes active by exchange, and a near-quantitative transfer of radiochlorine into the chlorine phase is achieved.

The fact that interchange occurs rapidly between a halogen and its corresponding halide ion was demonstrated experimentally (*2, 3, 5, 6*) several years ago. Halford (*4*) later explained this mechanism of interchange as a formation and decomposition of the trihalide ion and established a definite lower limit for the velocity of the interchange.

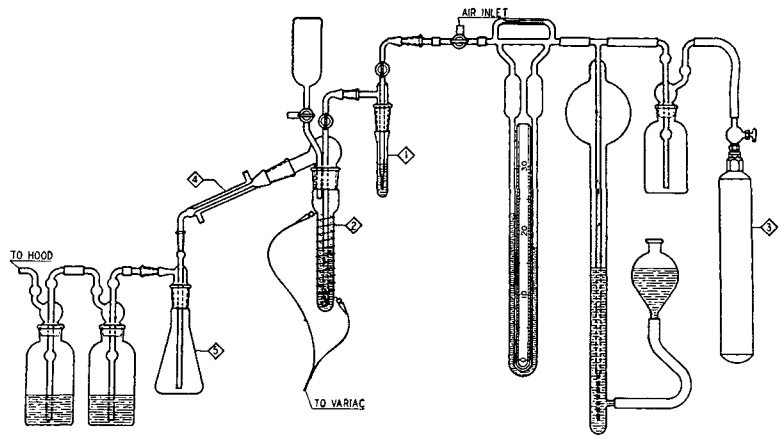


Figure 1. Chlorination Apparatus

The apparatus used for the chlorination is shown in Figure 1.

Place 15 ml. of benzene in the benzene reaction tube (tube 2, Figure 1). Using a 4-ml. pipet to which is attached a hypodermic syringe, place 4 ml. of aqueous radioactive 0.2 *N* hydrochloric acid containing 12 microcuries of chlorine-36 in the chlorine exchange tube (1, Figure 1).

Pass ordinary chlorine from the cylinder (3, Figure 1) for 30 minutes through the system up to the tube containing the radioactive hydrochloric acid in order to displace all the air in the system. Then, open the stopcock above the radioactive hydrochloric acid tube and bubble ordinary chlorine into the hydrochloric acid at the rate of 0.1 gram per minute for 6 minutes. Through an exchange reaction, the radioactive ionic chlorine in the aqueous hydrochloric acid exchanges instantly and nearly quantitatively with ordinary chlorine, so that molecular radioactive chlorine along with excess ordinary chlorine passes into the benzene reaction tube and becomes dissolved in the benzene.

After all the chlorine has passed into the benzene, place a 150-watt lamp 3 inches from the center of the benzene and allow it to remain there until the yellow-green color disappears. The reaction is then complete.

Introduce a stream of air through the bubbler in the benzene tube, apply heat to the coil, and distill the benzene. The air stream will flush the vapors through the condenser. About 1 gram of solid crude radioactive benzene hexachloride remains after removal of all the benzene. Dry the cake in a 75° vacuum oven to remove any remaining benzene.

Extraction of Gamma Isomer. Extract the gamma isomer from the cake with 2 ml. of *n*-hexane saturated with nitromethane by heating to the boiling point and stirring thoroughly. Decant the extract into a 50-ml. beaker. Repeat the extraction. Wash the spent cake with 2 ml. of cold *n*-hexane and combine the wash with the two extracts. Evaporate the solvent using a heat lamp placed about 8 inches above the beaker. After the solvent is removed, the gamma oil remains.

Final Preparation of Labeled Pure Gamma Isomer. Add 3.5 grams of pure unlabeled gamma isomer to the gamma oil obtained above. Dissolve the mixture in 16 ml. of 95% 3A ethyl alcohol by heating and stirring. After all the material dissolves, cool to 20° C. with constant stirring. Allow the slurry to stand in the bath for 15 minutes after crystals appear. Filter the crystals and wash with ethyl alcohol. The melting point of the dried crystals is 112.0–112.8° C.

Repeat the recrystallization at least two more times to be assured of removing all minute traces of benzene hexachloride isomers other than gamma. Dry the final crystals for 3 hours at 70° C. in a vacuum oven to remove all traces of solvent. The labeled standard is now ready for use.

DETERMINATION OF GAMMA ISOMER

The apparatus used in isolating the sample is shown in Figure 2.

Weigh approximately 120 ±5 mg. of the labeled standard into a tared 15 × 50 mm. shell vial and add approximately 1000 ±5 mg. of the unknown technical grade benzene hexachloride. Both the labeled standard and the unknown must be weighed accurately to 0.1 mg.

Add 1.2 ml. of perchloroethylene, place a cap (made from a 5-ml. beaker cut in half) on the vial, and insert the vial into the well of a 115° C. perchloroethylene heating bath (1, Figure 2). Allow the vial to remain in the bath for 15 minutes and stir the mixture occasionally to dissolve all the gamma isomer. Not all of the crude sample will dissolve.

Cool the mixture in the 20° C. water bath (3, Figure 2) for 30 minutes with occasional stirring to allow crystallization of isomers other than gamma. Leave the cap on during the crystallization.

Tare a 15 × 50 mm. shell vial and place in a Niederl-Niederl sulfur filtration apparatus (2, Figure 2). Filter the supernatant liquid from the crystallization through a filter stick into the tared vial. Wash the crystals by adding 0.3 ml. of perchloroethylene and cooling to 20° C. while stirring. Filter the wash into the vial containing the original filtrate.

Place the vial containing the filtrate and wash in an evaporation tube inserted in the top of the heating bath and evaporate the solvent, using a stream of air directed at the surface of the supernatant solution. Adjust the air stream so that splashing will not occur. Most of the perchloroethylene will be evaporated in 30 minutes. Weigh the residue which is the gamma oil. The usual yield of gamma oil at this point is 300 to 450 mg.

Crystallize the gamma oil by dissolving in 0.8 ml. per gram of a 1 to 1 mixture of 1,4-dioxane and *n*-butyl alcohol while heating and stirring until a homogeneous solution is obtained. Cool at 20° C. for 15 minutes in the water bath, then scratch the walls of the vial to induce crystallization. After the crystals appear, allow the slurry to stand in the bath for 10 more minutes, then filter in the Niederl-Niederl filtration apparatus. Wash the crystals with about 5 drops of cooled *n*-butyl alcohol.

The melting point of the crystals ranges from 100° to 112° C. after drying for 30 minutes in a 75° C. vacuum oven.

Recrystallize the material from *n*-butyl alcohol, using approximately 4 ml. of solvent per gram of crystals, by dissolving, then cooling to 20° C. as before. Filter the crystals, wash with about

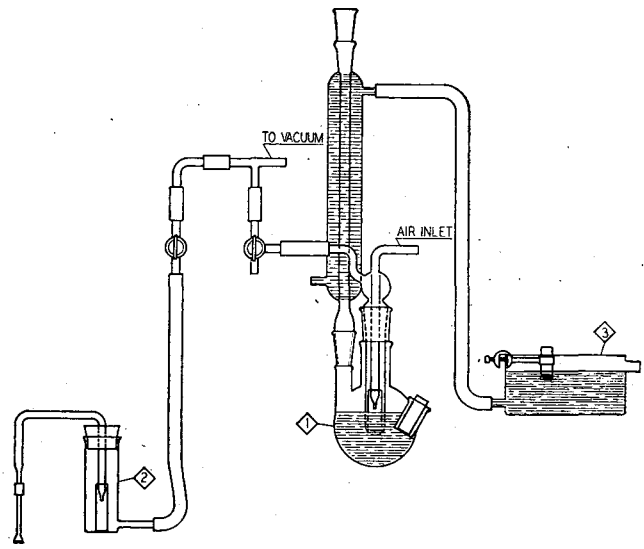


Figure 2. Sample Isolation Apparatus

3 drops of *n*-butyl alcohol, then dry for 30 minutes in a 75° C. vacuum oven. Repeat the recrystallization, using 3 ml. per gram of 95% 3A alcohol. Dry the crystals in a 75° C. vacuum oven for 2 hours.

A yield of about 50 mg. is usually obtained, melting at 112.0–112.8° C. If the melting point is in this range, the crystals are ready for counting. If not, the recrystallization must be repeated.

Table I. Precision

(Six Cl-36 analyses of technical BHC)

Sample No.	% Gamma
1	14.1
2	13.8
3	13.9
4	13.7
5	14.0
6	13.7
Mean	13.9
Range	0.4
Standard deviation	±0.15

Table II. Analyses of Synthetic Mixture

(Cl-36 analysis of a synthetic technical grade BHC)

Sample No.	Analyst[a]	Gamma Found, %
1	1	13.9
2	1	14.0
3	2	13.9
4	2	13.9
5	2	13.9
6	3	14.1
Average value	14.0	
Range	0.2	
Standard deviation	±0.09	

[a] Analysts 1 and 2 were experienced in running the analysis. Analyst 3 was not an analytical chemist and had never performed such an analysis or made any previous practice runs.

COUNTING PROCEDURE

Counting is done in solution. A thin-walled glass, liquid-jacketed counter tube (25 mg. per sq. cm., 10-ml. capacity) is used, shown in Figure 3.

A background count should be taken before counting a sample, with the counter tube filled with the same solvent used to dissolve the sample. This value must be subtracted from the count of both the sample and standard.

Accurately weigh the isolated pure gamma sample (to the nearest 0.1 mg.) into a 12-ml. snap cap vial, add exactly 10 ml. of acetone, and shake until all the sample is dissolved. Siphon the solution into the counter tube with a hypodermic syringe and count for about 15,000 total counts.

After counting the sample, flush out the tube three times with fresh acetone each time, then siphon dry. Check background again for 10 minutes to make sure the tube is decontaminated.

In a like manner prepare a solution of 50 mg., accurately weighed, of the original standard and count to the same approximate total count as the sample.

Calculate the results using the formula given below.

Calculations. Use the following equation for calculating the results:

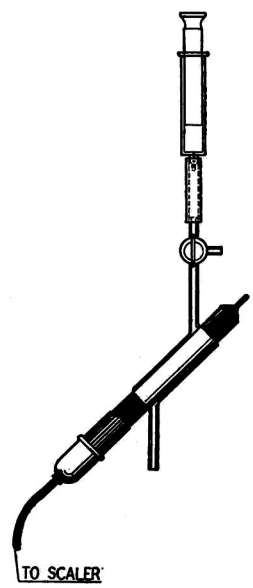


Figure 3. Counting Apparatus

Model J. T., N. Wood Counter Laboratory, 5491 Blackstone Ave., Chicago 15, Ill.

Table III. Determination of Gamma Isomer Content of AOAC Samples (*1*)

Method of Analysis	% Gamma (Average) Sample 1	Sample 2	Sample 3
Partition chromatography	13.4	1.52	48.2
Infrared	13.2	1.48	50.7
Polarography	13.6	1.67	47.8
Cl-36 method	12.9	1.42	50.5

$$X = \frac{A(B - C)}{C}$$

where

X = mg. of gamma benzene hexachloride in sample
A = mg. of radioactive standard added to sample
B = specific activity of the standard, or counts per minute of standard/mg. of standard counted
C = specific activity of the isolated sample, or $\frac{\text{counts per minute of isolated sample}}{\text{mg. of sample counted}}$

EXPERIMENTAL RESULTS

Table I shows the precision of the analysis. Six consecutive gamma determinations were made on a composite batch of technical grade benzene hexachloride which had been thoroughly blended. All analyses were run by the same analyst.

Table II shows the results of the analyses of a synthetic mixture of the alpha, beta, gamma, delta, and epsilon isomers, and heptachloride present in portions comparable to technical grade benzene hexachloride. The calculated gamma content was 14.0%.

Samples were assayed by several methods in a cooperative arrangement by a number of benzene hexachloride suppliers. Average values by each method are shown in Table III.

Another AOAC sample of technical benzene hexachloride distributed for infrared analysis had an average gamma isomer content of 13.24%. Chlorine-36 results showed 13.28%.

DISCUSSION

The isolation of the sample in an isotope dilution method requires simple technique, as the isolation does not have to be quantitative. The only quantitative operations required are weighing the standard and unknown, weighing the final isolated sample, and counting.

This analytical technique can be applied to benzene hexachloride samples having a wide range in gamma content. The weight of the unknown sample to be analyzed should be increased or decreased according to its estimated gamma content, so that the ratio of labeled gamma added to ordinary gamma in the sample will approximate the ratio described in this procedure.

ACKNOWLEDGMENT

The authors are deeply indebted to Cecil Carr, Commercial-Solvents Corp., for his valuable aid in working out a semimicro-method for isolating the pure gamma isomer from crude benzene hexachloride.

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Automatic Combustion Apparatus for Determination of Sulfur and Halogen

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In order to achieve the advantages of automatic operation, an automatic quartz tube combustion apparatus has been developed for the determination of sulfur and halogens in organic materials. The sample is vaporized in a stream of nitrogen and combustion occurs in the high temperature zone of the combustion tube, where a stream of oxygen is injected. A thermocouple, located just beyond the point at which oxygen is introduced, senses the heat generated by the combustion of the sample vapors and controls the amount of heat that is applied to cause vaporization of the sample. The apparatus reduces the training which must be given the operator, eliminates improper combustions resulting from errors in judging the volatility of samples, and automatically burns each sample at the maximum safe rate. An operator can complete 15 to 25 analyses per 8-hour day with virtually no possibility of losing an analysis because of improper combustion.

THE quartz tube combustion method (*1*) is widely used in the petroleum industry for determining sulfur and halogens in organic materials. In this method the sample, contained in a combustion boat, is vaporized in a stream of air by gradually applying heat to the sample boat. This technique requires the constant attention of the operator, and his experience and training are important factors in achieving properly controlled vaporization of the sample.

In attempts to design an apparatus which would allow more rapid combustion and would facilitate the combustion of volatile materials, a unit was constructed in which the sample was vaporized in a stream of nitrogen and the vapors were mixed with oxygen within the heated zone of the combustion tube. The observation that an intense flame resulted in the zone of admixture of oxygen and sample vapors suggested the possibility of using the flame temperature as a measure of the rate of sample vaporization. In preliminary tests a thermocouple was located in the flame and the temperature indicated by a pyrometer was used to guide the rate at which heat was manually applied to vaporize the sample. The direct relationship found between the flame temperature and sample vaporization rate suggested that the former could be used as the basis for automatic control of the latter. As a result of further investigation along these lines, an apparatus was developed which provides completely automatic sample combustion.

Combustion is carried out in a horizontally mounted quartz tube, a portion of which is maintained at 1000° C. The sample is placed in the cool zone of the tube and rapidly heated by application of full line voltage to a bare wire coil on the outside of the tube. Sample vapors are swept into the heated zone by a stream of nitrogen and mixed with a large excess of oxygen, at which point they burn with an intense flame. The rate of sample vaporization is controlled by a thermocouple located in this flame. The thermocouple, by means of an amplifier and relay circuit, switches the heater off and turns on a cooling air blast, or switches the heater on and turns off the air blast, as the flame temperature goes above or below the control point. Vaporization is controlled in this manner until the heater remains on for a 5-minute period, after which control is transferred to a 2-minute program controller. This removes the sample heater from the amplifier circuit and maintains it at full heat, causes oxygen to be passed over the sample boat to burn out any carbonaceous residue and, at the end of 2 minutes, sounds a buzzer and places the apparatus in a stand-by condition for the next sample. The desired constituents are absorbed from the gas stream and measured in the usual manner (*1*).

DESCRIPTION OF APPARATUS

A photograph of the apparatus is shown in Figure 1.

The cabinet is 23 inches long, 12.5 inches deep, and 11 inches high. There is no bottom, and cooling is promoted by raising the cabinet above the table with rubber feet and providing louvres at the top of the rear panel. The front panel is of Bakelite with the upper section at a 60° angle to make meter reading and switch manipulation more convenient.

Construction of the quartz combustion tube, its mounting, and furnace are shown in Figure 2.

A shatterproof glass guard protects the operator from quartz fragments, in the event that mismanipulation of the apparatus results in an explosion. The absorber is held in a flexible socket mounting which allows adjustment for variations in the dimensions of both the quartz tube and glassware. A vertical pipe carries the vacuum supply to the top absorber, so that the connection to the glassware can be made with a short piece of flexible tubing.

The left 9 inches of the front panel mounts the control unit, which can be independently withdrawn from the cabinet by means of the handle on the lower panel. Those electrical components not directly associated with the control unit, such as the trans-

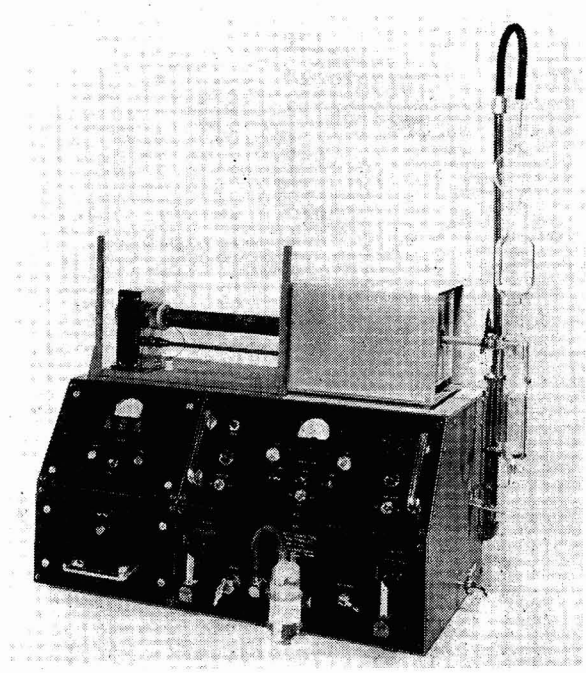


Figure 1. Apparatus

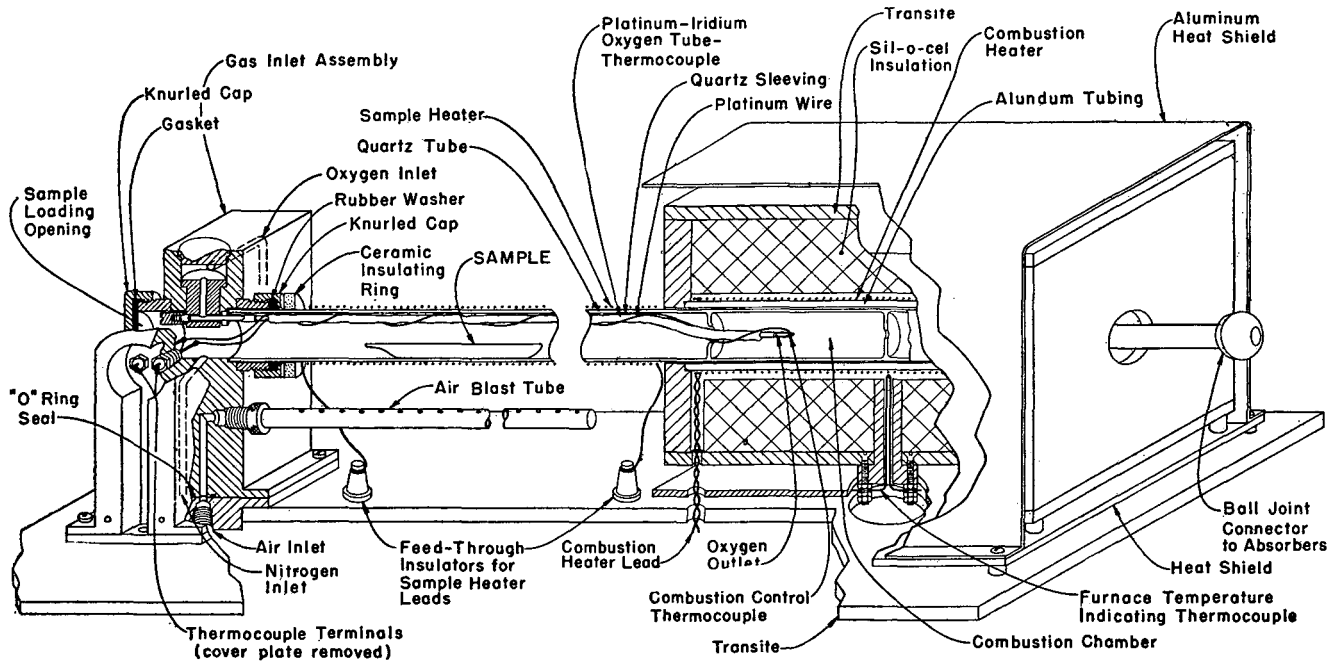


Figure 2. Furnace and Combustion Tube Assembly

former and switch for furnace temperature control, millivoltmeter for furnace temperature indication, program timing unit and relays, switches, fuses, pilot lights, and the starting push-button, are mounted on the upper right 14-inch section of the front panel. This unit is also fitted with panel handles and plug-in electrical connections which permit it to be easily withdrawn from the cabinet for servicing. The gas flow indicators and control valves are located on the vertical section of the front panel. Solenoid valves and copper tubing interconnecting the components of the gas flow system are located behind this panel and below the unit containing the furnace controls. All gas and electrical connections are at the rear of the cabinet.

Gas Flow System. The gas flow system is shown in Figure 3.

Nitrogen and oxygen at 5 pounds per square inch are introduced into the rear of the apparatus. Oxygen is introduced into the heated zone of the combustion tube through the long platinum-iridium tube, which also serves as one leg of the control thermocouple. Rotameters with self-contained needle valves are used to regulate the flow of oxygen and nitrogen. Vacuum is adjusted, using the panel-mounted vacuum control valve, so that it slightly more than accommodates the combined nitrogen and oxygen flows. At proper adjustment, a slow stream of air enters the system through the glass bubbler. Automatic application of vacuum and cooling air and selection of gases are achieved through the use of solenoid valves. A toggle-action valve permits the vacuum solenoid to be by-passed so that vacuum can be applied to the absorbers during transfer of the absorbing solution.

Combustion Control. A wiring diagram of the combustion control system is shown in Figure 4.

When the start button is momentarily depressed, relay 1 is energized and is locked in through cam 1 of the program controller (Type MC4 with A12 gear, Industrial Time Corp., Newark, N. J.). The start button circuit receives power through the amplifier power switch, which ensures operation of the control amplifier before the sample can be heated. The contacts on relay 1 connect power to the sample heater under control of relay 2 and amplifier relay 3, and to the vacuum, nitrogen, and secondary oxygen solenoids. The vacuum and secondary oxygen are under control of relay 1, while the nitrogen solenoid is under the further control of program controller cam 1.

The sensitive element is a platinum–platinum-iridium thermocouple formed between a No. 22 gage platinum wire and a finger-like extension of the platinum-iridium oxygen supply tube (see Figure 2). The electromotive force from the couple at the control temperature is balanced by an equal voltage of opposite polarity obtained from a local battery circuit. The local battery circuit is standardized by setting the voltage across the divider network with coarse and fine rheostats to 1 volt, as indicated by a small panel meter. A separate adjustment is provided for setting the operating flame temperature.

The difference voltage between the reference circuit and the thermocouple is converted to alternating current by a Brown vibrating converter and coupled to a two-stage, high-gain R-C coupled amplifier by a Brown input transformer. The miniature amplifier tube, a dual triode Type 12AX7, and all of the amplifier components shown within the dotted line on the wiring diagram are mounted on a heavy brass plate which is suspended from the chassis by four rubber shock mounts to protect the circuit from vibration-induced transients.

The output of the amplifier is capacitively coupled to a Type 2D21 miniature thyratron, in the anode circuit of which is a double-pole, double-throw relay (relay 3) which supplies power to the sample–cooling air solenoid valve in its normal position and power to the sample heater and to the timing relay in its energized position. A signal-limiting germanium diode is included in the input circuit of the thyratron to prevent undesired relay action from large amplitude signals. The sensitivity is such that clean-cut relay operation is obtained for an input signal change of approximately 4 microvolts.

The direct-current anode voltage source for the amplifier must be free of voltage fluctuations. A separate small transformer and selenium rectifiers in a voltage doubler circuit, followed by an R-C filter and two Type OA2 voltage regulator tubes, provide the required stability.

When relay 3 is energized, by the reference voltage being greater than the electromotive force generated by the control thermocouple (a condition resulting when no flame exists), the sample heater and time-delay relay receive power and the cooling air solenoid is de-energized. The sample starts to vaporize when heated, and the vapors are carried into the hot zone of the combustion tube by the nitrogen stream. As the vapors enter the hot zone they are mixed with oxygen and a flame results. The control thermocouple is located in the flame and quickly generates an electromotive force which, when it exceeds that of the reference electromotive force, shuts off the sample heater and time-delay relay and turns on the distributed air blast which rapidly cools the sample below the vaporization temperature. Because the amplifier relay 3 connects the heater in its energized position, the control amplifier is "fail safe," applying cooling air on electron tube failure. When the flame subsides, the thermocouple output decreases below the control value, resulting in the energization of relay 3, which shuts off the cooling air and starts a new heating and timing cycle. This action is repeated until a heating cycle lasts 5 minutes.

The timing device by which completion of the sample vaporization cycle is determined is a Cramer Type TC-5M time-delay relay. This unit consists of a synchronous motor geared down to

drive a cam which actuates a switch. A spiral spring is wound up as the cam turns and returns the cam to the starting position when the energizing current to the motor is interrupted. Preliminary tests showed that all materials normally encountered were completely vaporized or reduced to a carbonaceous residue when a 2-minute time delay was used and a 5-minute time delay was arbitrarily selected to provide a large margin of safety. At the termination of the 5-minute heating period the delay relay energizes relay 2 and the program controller motor. Relay 2 locks in under control of relay 1 and removes the sample heater control from amplifier relay 3 and places it on full heat under control of relay 1.

When the program controller starts its 2-minute cycle, it locks in under control of cam 3 while cam 1 switches power from the nitrogen solenoid to the oxygen solenoid. This stops the nitrogen flow over the sample and substitutes oxygen, which burns out any carbonaceous residue remaining in the sample boat. Near the end of the 2-minute program controller interval, cam 2 momentarily energizes a warning buzzer and opens the locking circuit on relay 1. A few seconds later cam 3 opens the program controller motor circuit, which restores the entire apparatus to starting status. Had the air switch been closed, sample cooling would have commenced at the end of the program cycle and continued until the operator manually opened the switch or started another run.

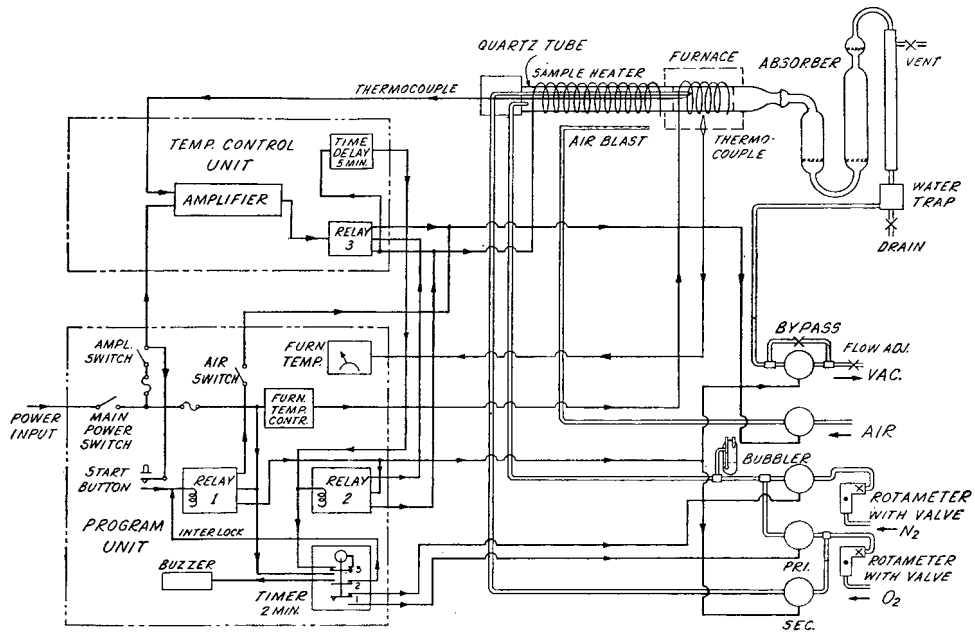


Figure 3. Block Diagram of Automatic Quartz Tube Combustion Apparatus

Sample Heater and Furnace. The sample heater consists of 34 feet of No. 18 Chromel A wire, wound on a mandrel so that it fits loosely on the quartz tube. The combustion furnace element is wound on an Alundum tube, also of Chromel A wire (No. 22), approximately 40 feet wound at 22 turns per inch for 1 inch on each end, with the balance of the $7^3/_8$-inch length wound at 18 turns per inch. This tube is insulated with fireclay bricks, bored out to receive it, and the bricks are housed in a Transite box which is further insulated with a spaced aluminum shield.

The furnace can be adjusted to the operating temperature, approximately 1000° C., for line voltages from 105 to 125 volts. A radio-type filament transformer is used as an autotransformer and a 5-position rotary switch permits line voltage, or line voltage ±5 and 10 volts, to be connected to the furnace.

Quartz and Glass Parts. The quartz combustion tube is shown in Figure 2.

The tube is 535 mm. in total length; 440 mm. is 25 mm. in outside diameter and the remainder is 12 mm. in outside diameter. A baffle, with a central hole 7 mm. in diameter, is located 310 mm. from the entrance end so as to be just inside the furnace. The oxygen supply tube is 2.0 mm. in inside diameter × 2.5 mm. in outside diameter and 340 mm. long and, with its thermocouple, is placed a short distance through this hole. A second baffle, with a central hole 5 mm. in diameter, is located 375 mm. from the entrance end to promote complete mixing of the combustion gases. The combustion tube contains no packing.

The absorbers, spray traps, and absorber adapters are identical with those described previously (*1*). The 2-foot-long brass pipe which extends the vacuum line to the top of the glassware serves as a condenser which takes out droplets passing the glass trap and is provided with a vent which is used in the operations involved in transferring the absorbing solution. In addition, a metal trap with baffles is connected in series with the line and traps out any remaining water. The trap is provided with a convenient drain cock for emptying.

Adjustment of Operating Flame Temperature. The temperature at which the thermocouple generates sufficient electromotive force to actuate the control circuit is determined by a rheostat (see Figure 3) located on the front panel. An adjustable rather than a fixed operating temperature is employed because of the difficulty in exactly fixing the position of the thermocouple with relation to the flame. The proper setting of the rheostat is determined by burning a 1-gram portion of mineral oil in the apparatus and adjusting the rheostat during combustion so that the heating and cooling periods of each control cycle are approximately equal and combustion is completed in 17 to 20 minutes.

PROCEDURE

If sulfur is to be determined, introduce 30 ml. of 1.5% hydrogen peroxide solution into the lower (primary) absorber and 10 ml. into the upper (secondary) absorber. (While 3% hydrogen peroxide solution has been employed by others and is satisfactory, the 1.5% solution has adequate reserve capacity for any materials that might be encountered and there seems to be no need for use of a stronger reagent.) If halogen is to be determined, introduce 25 ml. of 2.5% sodium carbonate solution and 10 ml. of 6% hydrogen peroxide into the primary absorber, and place 10 ml. of water in the secondary absorber. Insert the sample boat into the combustion tube and slide it approximately

Table I. Determination of Sulfur and Halogen with Automatic Quartz Tube Apparatus

Material	Sulfur or Halogen, % Present	Found
Carbon tetrachloride	92.2	92.0
Gamma-benzene hexachloride	73.2	72.8
Monochlorinated paraffin wax	17.3	17.3
Monochlorinated paraffin wax + white oil		
Sample A	6.05	6.04
Sample B	0.64	0.69
Sample C	0.13	0.12
4,4-Dibromodiphenyl ether	48.9	48.5
		48.6
o-Iodobenzoic acid	51.2	51.7
m-Iodotoluene	58.2	58.6
Flowers of sulfur	100.0	98.9
		99.1
Diethyl sulfide	35.6	35.5
		36.0
		35.6
Benzyl disulfide	26.0	26.1
3-Sulfolanal	23.6	23.2
		23.3
Phenyl sulfide	17.3	17.4
Phenyl sulfoxide	15.9	16.0
		16.0
Benzyl sulfide + white oil		
Sample A	2.52	2.50
Sample B	1.00	0.98
Sample C	0.21	0.21

to the center of the sample heating section of the tube; replace the inlet cap. Depress the start button and set the flow of oxygen at 2.5 liters per minute, and the flow of nitrogen at 400 ml. per minute, and adjust the vacuum to draw a small stream of air through the bubbler. Combustion is completely automatic and the buzzer will sound to indicate completion of the combustion. The apparatus automatically resets and the cooling air blast turns on when the combustion cycle is complete.

When the combustion cycle is completed, disconnect the quartz tube from the adapter. Close the adapter with a ball joint plug, turn on the vacuum by-pass valve, and allow vacuum to be applied to the absorber. Turn off the vacuum valve and slowly bleed air into the system through the air inlet valve, allowing the liquid to be drawn from the secondary absorber into the primary absorber. As the pressure equalizes, remove the spray trap, rinse it, and collect the washings in the secondary absorber. After all the liquid has been drawn into the primary absorber, rinse the secondary absorber, using not more than 20 ml. of water. Finally, remove the secondary absorber and wash the ground joint, both inside and out. Remove the stopper from the adapter and rinse both the stopper and adapter with a small quantity of water, collecting the washings in the primary absorber. For the determination of sulfur, in the absence of other acid-forming elements such as halogens, titrate the sulfuric acid collected in the absorber with standard caustic solution; for the determination of halogen, titrate the halide ion content of the absorbent by the Volhard method (*1*).

DISCUSSION

The above method and apparatus have been applied to a great variety of materials; Table I shows results typical of those obtained for samples containing known amounts of sulfur or halogen. These data indicate that an accuracy of 99% or better may be expected for materials containing more than 5% sulfur or halogen. In the lower concentrations, sulfur or halogen can generally be determined to ±0.03%.

The sampling techniques employed with the automatic unit differed somewhat from those used with the manually operated apparatus (*1*). Solids or heavy liquids were weighed directly into open boats. Liquids which tended to "creep" from the combustion boat were delivered from a small weighing pipet to a boat placed partially inside the combustion tube and the boat was then quickly inserted into the tube. Sample tubes with capillary stems were found to be unsatisfactory for sampling volatile liquids because the liquid was expelled too rapidly from

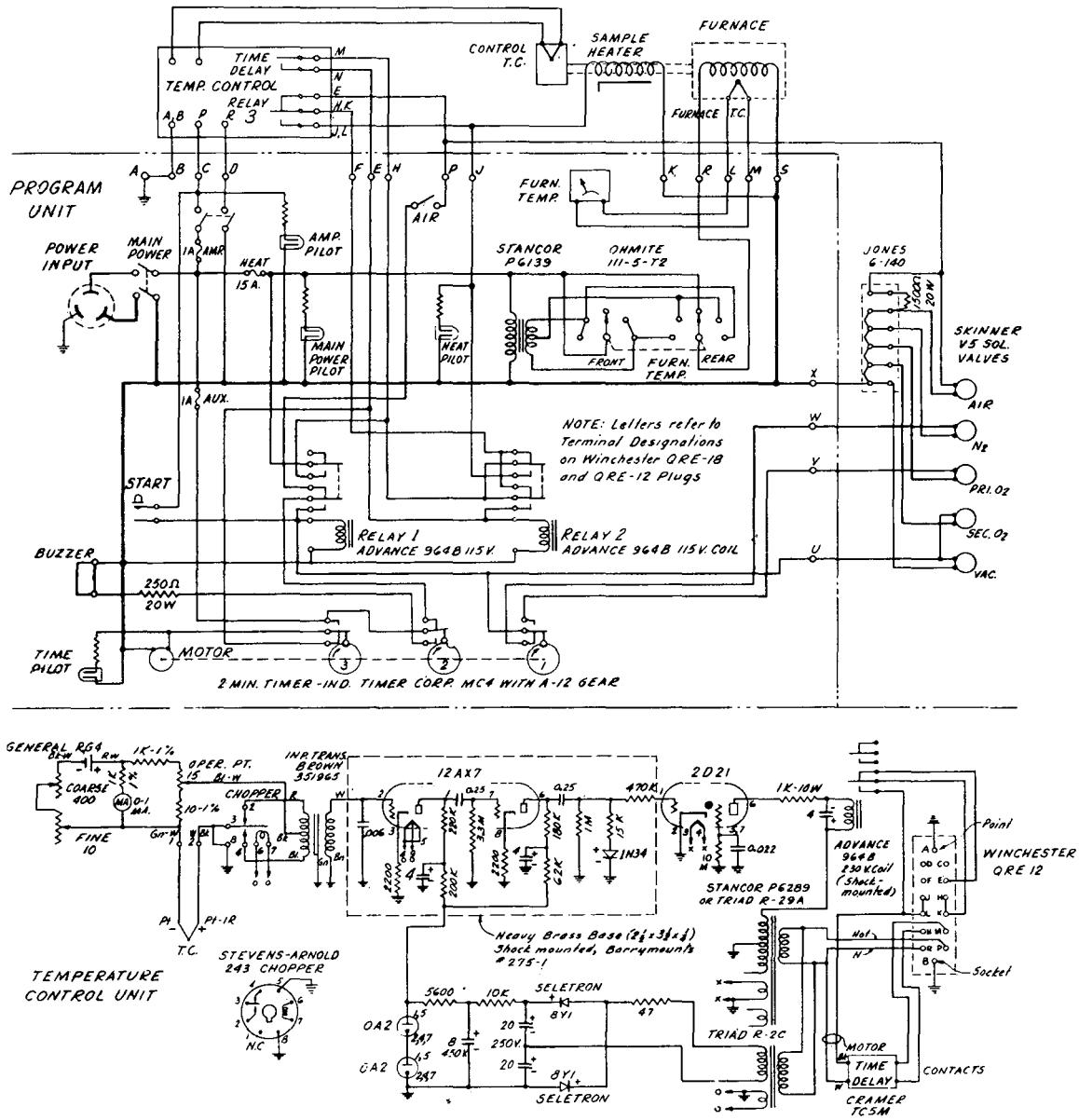


Figure 4. Wiring Diagram of Automatic Quartz Tube Combustion Apparatus

the tube, resulting in incomplete or too rapid combustion. This difficulty was overcome by placing the sample in size 00 gelatin capsules which were half-filled with 100- to 200-mesh silica gel. The silica gel served to adsorb the sample and, thus, to reduce its vapor pressure; without the silica gel, sample vapors escaped from the capsule. The capsule containing silica gel was weighed, the sample dripped onto the silica gel from an eyedropper, the capsule capped, and reweighed, and the loaded capsule placed in a porcelain boat. The capsule was then punctured with a pin and the boat quickly inserted into the combustion tube. As gelatin contains nitrogen, a small amount of nitric acid was formed during combustion of the capsules, necessitating a correction when sulfur was measured by titration of sulfuric acid. The correction, approximately 0.6 ml. of 0.06 N sodium hydroxide solution, was established by titrating the acid formed when empty capsules were burned in the apparatus. The capsules were sufficiently uniform in weight, so that the value of the correction did not vary significantly.

The time required for combustion varied from 6 minutes for 0.2-gram samples to 20 minutes for 1-gram samples. These times are considerably less than those required with the manually operated apparatus for comparable samples. The automatic operation permits the operator to weigh samples or to titrate absorber liquids while combustion is proceeding; and because of the rapidity of the combustion, an operator can complete from 15 to 25 determinations in an 8-hour working day. This productivity is, in effect, further increased relative to the manually operated apparatus because no determinations are lost with the automatic unit as a result of incomplete combustion.

Although the control and operating circuits of this unit are fairly complex, the apparatus has required very little maintenance service when used daily for many months. The principal maintenance operations have involved occasional replacement of the quartz tube and the small battery which serves to balance the thermocouple e.m.f.

ACKNOWLEDGMENT

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Extraction of Heteropoly Acids

Application to Determination of Phosphorus

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A study was made of liquid-liquid extraction to evaluate its applicability to separations of heteropoly acids. The efficiency of the extractions was measured by means of ultraviolet spectrophotometry. Molybdophosphoric acid is the most readily extracted of the acids tested. A method is recommended for determining phosphorus in steel utilizing extraction of molybdophosphoric acid with a 20% by volume solution of 1-butanol in chloroform. The method was successfully applied to National Bureau of Standards steel samples containing up to 1.4% manganese, 0.3% silicon, 1.0% chromium, or 0.2% vanadium.

STUDY of heteropoly acids has led to useful methods for the determination of phosphorus (*6*), arsenic (*5*), silicon (*7*), and germanium (*16*), among other things. The methods cited are similar in that the element being determined is the central atom of a heteropoly acid in which molybdate is the coordinated group.

A common drawback of these methods is that the presence of any of the central-atom elements other than the one being determined causes interference of such magnitude that the concentration of the interferer can be only a fraction of that of the desired constituent without seriously impairing the accuracy of the results. Since the methods under consideration are used for determinations of traces, this means that the interferers must be completely absent when the measurements are made. Interference by soluble silica is especially common, as aqueous solutions in contact with glass are contaminated in a short time.

Using the molybdovanadophosphoric acid method (*17*), one can measure 10 p.p.m. of phosphorus in the presence of 50 p.p.m. of arsenic or 500 p.p.m. of silicon.

In several instances selective extraction of heteropoly acids has been used to effect the separations necessary to overcome interferences. Consequently, a systematic study of liquid-liquid extraction was undertaken to evaluate the general applicability of this type of separation.

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APPARATUS AND REAGENTS

Absorbance measurements were made with a Cary spectrophotometer, Model 10-11M. The wave-length scale was calibrated frequently with a mercury arc using the lines at 280.4 and 313.2 mμ. The photometric scale was calibrated with cobalt blue, copper green, selenium orange, and carbon yellow glasses issued by the National Bureau of Standards. The slit width of the instrument gave a half-intensity band width of approximately 0.1 mμ throughout the spectral region used.

A matched pair of 1-cm. quartz cells with ground-glass stoppers, supplied by the American Instrument Co., was used.

The organic solvents used for extraction were of technical grade. All other chemicals were of reagent grade.

Aqueous solutions were stored in hard-rubber or polyethylene bottles to prevent contamination by silica.

GENERAL STUDY OF EXTRACTION OF HETEROPOLY ACIDS

Literature Survey. Liquid-liquid extraction has been used to effect separations of heteropoly acids in a variety of applications. For example, Jacobs extracted excess tungstophosphoric acid with 1-pentanol after using the acid as a protein precipitant (*13*). Wu extracted molybdophosphoric acid into ethyl ether as a means of purifying the acid (*31*).

If molybdophosphoric acid is shaken with ethyl ether, three layers form. The volume of the viscous, deep yellow, bottom layer is proportional to the amount of phosphorus present (*8*). Poussigues applied a similar method to the measurement of arsenic (*22*).

Scroggie found that esters, ketones, aldehydes, and ethers are good extractants, but that carbon disulfide, carbon tetrachloride, chloroform, benzene, and toluene are not (*26*). Keggin stated that oxygen-containing materials are good solvents for heteropoly acids (*14*).

Stoll employed extraction into ethyl acetoacetate to concentrate molybdophosphoric acid and to separate it from molybdosilicic acid (*28*). Hure and Ortis measured molybdosilicic acid after removal of molybdophosphoric acid with ethyl acetate (*12*). Butyl acetate can also be used for this separation (*18*).

2-Methyl-1-propanol has been used to extract molybdophosphoric acid (*2, 3, 27*). Rainbow prefers 3-methyl-1-butanol for this purpose (*23*). Schaffer *et al.* recommended 1-octanol in preference to 3-methyl-1-propanol because the octanol extracts less extraneous material (*25*).

A method for determination of arsenic is based on extraction with 1-butanol (*29*).

Molybdovanadophosphoric acid has been extracted with 3-methyl-1-butanol and ethyl ether (*20*) and mixtures of 1-butanol and ethyl ether or 1-butyl acetate, 1-butanol, and ethyl ether (*15*).

A mixture of 1-butanol and chloroform selectively extracts molybdophosphoric acid in the presence of arsenic and silicon (*9, 21*). The procedure can be extended by treating the residual aqueous solution with a mixture of 1-butanol and ethyl ether to extract molybdoarsenic acid and finally with 1-butanol to extract molybdosilicic acid (*1, 10*).

Purpose of Investigation. Because a number of heteropoly acids are yellow, it seemed of interest to study the absorption spectra in the ultraviolet region of the spectrum. This has not been done in the past, with the exception of Boltz's study of molybdophosphoric acid (*6*), presumably for two reasons.

The first reason is the high absorptivity of sodium molybdate itself in the ultraviolet region. The development of maximum absorptivity of heteropoly acids containing molybdate as the coordinated group depends upon the presence of a large excess of sodium molybdate, which interferes with absorptiometric measurements. By extracting the heteropoly acids with organic solvents the acid can be separated, leaving the sodium molybdate in the aqueous solution and overcoming the interference.

The second reason was lack of the necessary equipment. With the Cary spectrophotometer now available, it is possible easily and quickly to collect continuously recorded absorption spectra from 200 to 400 mμ.

Using this tool, extraction procedures were studied, noting the effect of type of solvent and solution conditions such as concentration and acidity.

Experimental Work. Solution Conditions. The heteropoly acids chosen for study were molybdophosphoric acid, molybdoarsenic acid, molybdosilicic acid, and molybdogermanic acid. They were all prepared in solution by mixing appropriate amounts of sodium molybdate, hydrochloric acid, and potassium dihydrogen phosphate, arsenic acid, sodium silicate, or sodium germanate. The sodium silicate was reagent grade $Na_2SiO_3.9H_2O$. The sodium germanate was prepared by a sodium carbonate fusion of germanium dioxide obtained by hydrolyzing germanium tetrachloride.

Several factors were considered in establishing the conditions under which to conduct the experiments. Dilute solutions of heteropoly acids suitable for absorptiometric measurements require a large excess of molybdate ion to displace to the right reaction (*1*), as formulated by Rosenheim (*24*).

$$X^nO_a^{(2a-n)-} + 12MoO_4^{--} + (24 + 2a - n)H^+ \longrightarrow H_{(12-n)}X(Mo_2O_7)_6 + (6 + a)H_2O \quad (1)$$

[X may be P(V), As(V), Si(IV), or Ge(IV)]

The excess is critical and must be accurately reproduced in each preparation, as molybdic acid itself is extracted by some solvents and absorbs in the ultraviolet region. The molybdate concentration was set at a level high enough so that heteropoly acids could be formed but low enough so that the absorption of molybdic acid did not overshadow the effects which were under investigation.

The concentration of the central atom was chosen so that absorption beyond that of the molybdic acid is great enough to be measured.

These two solution conditions having been arbitrarily established, the optimum acidity was determined by tests of extraction using 1-butanol as extractant. That hydrochloric acid concentration was considered optimum which gave the highest absorbance at 300 mμ for the extract of the heteropoly acid when the extract of a solution of the same sodium molybdate concentration and acidity was used in the reference beam.

Table I lists the conditions which were judged to be optimum and were used throughout the study of various solvents. The aqueous solutions had volumes of 25 ml. in the cases of phosphorus and arsenic, and 20 ml. in the cases of silicon and germanium.

Procedure. The aqueous solution was prepared in a beaker and then poured into a 125-ml. separatory funnel. Ten milliliters of the solvent to be tested was placed in the beaker, swirled, and then poured into the separatory funnel. The funnel was shaken for 30 seconds and the layers were allowed to separate. If the solvent was lighter than water, the aqueous solution was drawn off into the beaker and the organic layer was drained into a 25-ml. volumetric flask. If the solvent was heavier than water, it could be drained directly into the volumetric flask. In either case, the extraction was repeated with 10 ml. more of solvent. The second portion of solvent was added to the first and the flask was filled to the mark with more solvent.

If the solvent which had been in contact with the aqueous solution was cloudy because of suspended water droplets, in every case the addition of fresh solvent to dilute to the mark of the volumetric flask caused the solution to clear. This difficulty can be minimized by carrying out the extraction with gentle rather than vigorous shaking.

Measurements. For each test three absorbance curves were recorded: (1) solvent *vs.* solvent as reference, (2) blank extract *vs.* solvent as reference, and (3) heteropoly acid extract *vs.* blank extract as reference. The wave-length range of the curves was from 400 mμ to the shortest wave length at which the solvent transmits enough energy to be usable.

Solvents Tested. The solvents were selected to include representatives of the classes alcohol, ketone, ester, ether, hydrocarbon, and chlorinated hydrocarbon.

Results and Conclusions. The shortest wave length at which the various solvents could be used for absorbance measurements varies from 215 mμ for ethyl ether to 335 mμ for 2,6-dimethyl-4-heptanone. For this reason, the absorbance values had to be compared at a wave length longer than 335 mμ. Table II lists the absorbances observed at 350 mμ using a reagent blank as the reference material, and the shortest wave length at which each solvent is usable.

Figure 1 shows spectrophotometric curves of 1-butanol extracts of the heteropoly acids studied. The shapes of the absorption spectra are similar in the other solvents tested.

Examination of Table II leads to several conclusions. The

Table I. Optimum Conditions for Extraction of Heteropoly Acids into 1-Butanol

Central Atom	Amount, γ	Molarity of Reagents	
		Na_2MoO_4	HCl
P	25	0.025	0.96
As	100	0.013	0.67
Si	100	0.010	0.15
Ge	100	0.010	0.15

Table II. Absorbance of Extracts of Heteropoly Acids at 350 Mμ

(Measured in 1-cm. cells with Cary spectrophotometer, using reagent blank as reference)

Solvent	Shortest Usable Wave Length, Mμ	A_{350} P, 25γ	As, 100γ	Si, 100γ	Ge, 100γ
1-Butanol	240	0.328	0.530	0.612	0.204
2-Butanol	260	0.258	0.518	0.270	0.208
2-Methyl-1-propanol	230	0.356	0.500	0.536	0.245
1-Pentanol	265	0.315	0.302	0.641	0.091
1-Hexanol	280	0.331	0.120	0.349	0.029
2,6-Dimethyl-4-heptanone	335	0.386	0.032	0.014	0.026
Ethyl acetate	250	0.295	0.088	0.005	0.003
1-Butyl acetate	255	0.310	0.020	0.002	0.006
Amyl acetate	280	0.310	0.030	0.059	0.120
Ethyl acetoacetate	330	0.384	0.617	0.400	1.140
Ethyl ether	215	0.307	0.093	0.004	0.003
2-Propyl ether	255	0.142	0.013	0.003	0.002
Chloroform	240	0	0	0	0
Carbon tetrachloride	250	0	0	0	0
Petroleum ether (30–60° C., b.p.)	225	0	0	0	0

esters listed are the most selective extractants of molybdophosphoric acid, 1-butyl acetate being the best of these. If a solvent will extract any heteropoly acid at all, molybdophosphoric acid is among those extracted. The properties of the four heteropoly acids studied are so nearly alike that most of the solvents are as good for extracting one acid as another.

A generalization can be made that of the solvents tested only those which contain oxygen serve as extractants. Possibly nitrogen-containing and sulfur-containing solvents could also be used.

ULTRAVIOLET ABSORPTIOMETRIC DETERMINATION OF PHOSPHORUS AS MOLYBDOPHOSPHORIC ACID

Phosphorus was the first element known to act as a central atom in a heteropoly acid (*4*), and it is looked upon as typical of the group of elements which can so function.

The absorptiometric determination of phosphorus is subject to interference if arsenic, silicon, or germanium is present, if one measures the absorbance of molybdophosphoric acid itself (*6*), or the corresponding heteropoly blue (*30*). The use of molybdovanadophosphoric acid as the measuring form partially overcomes these interferences (*17*).

The results of the general study of extraction were examined to see if some extraction operation can be used to circumvent this type of interference. The data of Table II suggest that 1-butyl acetate is the most highly selective of the solvents tested. The literature survey suggests that the 25% by volume solution of 1-butanol in chloroform used by Akkseev (*1*) and Filippova and Kuznetsova (*10*) will give highly selective extractions.

Several preliminary trials showed that the 1-butanol–chloroform solution is more desirable from the standpoint of ease of separation of the layers after extraction. The chloroform medium also seemed less likely to extract other colored inorganic materials, such as ferric chloride, which would be present, for example, during a steel analysis. For these reasons, the 25% by volume solution of 1-butanol in chloroform was chosen for detailed study.

The earlier workers recommended that the aqueous solution, from which up to 10 mg. of phosphorus as molybdophosphoric acid is to be extracted, be 0.5 *N* in nitric acid and contain 0.5 gram of ammonium molybdate in a total volume of 100 ml. As it was desired to study the application of ultraviolet absorptiometric measurements along with extractions and the absorptivity of molybdophosphoric acid is greater in the ultraviolet than in the visible region of the spectrum, lower concentrations had to be used in this work.

Optimum Conditions. The operations required to form molybdophosphoric acid, extract it, and measure it were examined by the following procedure to find the optimum conditions.

One milliliter of a solution containing 25γ of phosphorus per ml., as potassium dihydrogen phosphate, was treated with the desired amounts of 2 *N* hydrochloric acid and a 1.5% solution of sodium molybdate dihydrate and diluted to 25 ml. The solutions were then shaken with two successive 10-ml. portions of a 25% by volume solution of 1-butanol in chloroform. The extracts were combined and diluted to 25 ml., and their absorption spectra were measured with the Cary spectrophotometer in 1-cm. cells from 240 to 400 mμ using a reagent blank in the reference beam. The spectra, which are of the type shown in Figure 2, have an absorbance maximum at 310 mμ. This wave length was used to evaluate the effects of the variables.

It was found that the optimum conditions, when the 25% by volume solution of 1-butanol in chloroform was used as extractant, are achieved by adding 11 ml. of hydrochloric acid and 10 ml. of the sodium molybdate solution. The system follows Beer's law at 310 mμ up to 50γ of phosphorus.

The experimental work up to this point showed that Akkseev's method can be used to measure phosphorus satisfactorily. A few measurements, however, showed that this system is not free from interference by arsenic, silicon, and germanium.

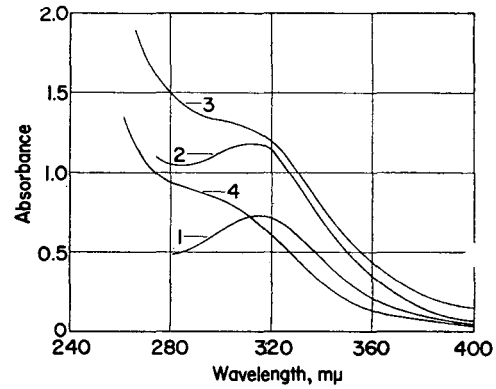


Figure 1. Absorption Spectra of 1-Butanol Extracts

1. Molybdophosphoric acid
2. Molybdoarsenic acid
3. Molybdosilicic acid
4. Molybdogermanic acid

Solutions prepared according to conditions shown in Table I. Measurements made with Cary spectrophotometer using 1-cm. cells, 0.1-mμ band width, and reagent blanks

Table III. Interferences of Heteropoly Acid-Forming Materials in Measurement of 25γ of Phosphorus at 310 Mμ

Element	Amount, Mg.	1-Butanol in Extractant, % 16.7	20.0	25.0
		Relative Error, %		
As	3	...	+2.0	+2.2
As	5	+2.0	+3.0	+6.3
Ge	1	+0.5	+0.5	+3.1
Ge	5	...	...	+12.0
Si	5	+0.3	+0.6	+0.6

Table IV. Effect of Proportion of 1-Butanol in Extractant on Sensitivity of Phosphorus Measurement

(Measurements of 25γ P made with Cary spectrophotometer using 1-cm. cells, with solvent in reference cell)

Proportion of 1-Butanol in Extractant, %	A_{310} 25γ P	Blank	25γ P − blank
100.0	>2.25	>2.25	Indeterminate
66.7	1.427	0.190	1.237
50.0	0.960	0.160	0.800
33.3	0.889	0.072	0.817
25.0	0.844	0.042	0.802
20.0	0.798	0.031	0.767
16.7	0.519	0.010	0.509
12.5	0.128	0.010	0.118
10.0	0.028	0.010	0.018

Table V. Statistical Study of Reproducibility of Measurement of 25γ of Phosphorus by Recommended General Procedure

x = individual values
n = 25 = number of values observed
$\sigma = \sqrt{\frac{\Sigma(x - \bar{x})^2}{n - 1}}$ = 0.00909 = standard deviation
$\sigma' = \sigma/c_2$ = 0.00937 = an estimate of true standard deviation of population to which measured values of x belong
c_2 = factor relating an observed σ for a given n to its σ' (*11*)
$\bar{x}$ = 0.81760 = average of observed values[a]
$\bar{x}' = \bar{x}$ = estimate of true mean of population to which measured values of x belong
R = range of samples = highest x value minus lowest x value

Using 3-sigma levels for calculating control limits for determinations made in duplicate:

Lower control limit for $R = 0 \times \sigma' = 0$
Upper control limit for $R = 3.69 \times \sigma' = 0.034$
Lower control limit for $\bar{x} = \bar{x}' - 2.12\sigma' = 0.798$
Upper control limit for $\bar{x} = \bar{x}' + 2.12\sigma' = 0.838$
Calculations based on methods given by Grant (*11*).

[a] It should not be construed that the absorbance measurements were made to five significant figures.

Proportion of 1-Butanol in Extractant. Experimentation to see what effect the proportion of 1-butanol in the extractant has on interferences and sensitivity gave the data of Tables III and IV. A high proportion of 1-butanol gives high interferences and high sensitivity, while a smaller proportion of 1-butanol gives low interferences but also low sensitivity. The use of an extractant which is a 20% by volume solution of 1-butanol in chloroform was considered to be the best compromise and was used in the rest of the study.

Because this extractant is different from the one used previously to find the optimum solution conditions, the effects of acidity and molybdate concentration were restudied.

ACIDITY. Twelve milliliters of 2 *N* hydrochloric acid gives the optimum acidity. Substitution of an equivalent amount of nitric acid causes the absorbances of both the phosphorus solution and the reagent blank to be increased slightly, but the sensitivity is unaltered. An equivalent amount of sulfuric acid gave low results.

MOLYBDATE CONCENTRATION. It was decided to continue using 10 ml. of the 1.5% sodium molybdate dihydrate solution.

MIXED REAGENT. The amount of reagents added must be measured with a pipet to obtain acceptable reproducibility. The addition of 10.0 ml. of a mixed reagent which is both 1.5% in sodium molybdate dihydrate and 2.4 *N* in hydrochloric acid gives the concentrations previously judged to be optimum.

VOLUME OF AQUEOUS SOLUTION. As acidity and molybdate concentration are critical, the volume of the aqueous solution should not vary by more than ±2 ml. from 25 ml.

EXTRACTION TECHNIQUE. In order to get maximum absorbance readings, it is necessary to shake the solutions together for at least 60 seconds during each of the two extractions.

BEER'S LAW CONFORMANCE. Beer's law is followed at 310 mμ for 0 to 50 γ of phosphorus. The molar absorptivity is 24,400 liters per mole cm.

STABILITY. The solutions are stable for at least 14 days when stored in glass-stoppered flasks in ordinary light.

INTERFERENCES. The procedure for study of interferences was to mix 1 ml. of a solution containing 25γ of phosphorus per ml., as potassium dihydrogen phosphate, with the desired amount of a solution containing the suspected interferer. This solution was diluted to 15 ml. and 10 ml. of the mixed reagent was added from a pipet. The solution was shaken for 60 seconds with 10 ml. of 20% by volume solution of 1-butanol in chloroform. After the layers had separated, the nonaqueous phase was drained into a 25-ml. volumetric flask, the extraction was repeated, the organic layer was added to the first extract, and the solution was diluted to the mark with fresh solvent. The absorbance was then measured at 310 mμ in 1-cm. cells with extractant in the reference cell. All tests were run in duplicate.

The existence or nonexistence of interference was judged by reference to control limits which were calculated from 25 samples containing no extraneous ions. The data are given in Table V. If the range of any duplicate pair exceeded 0.034, the values were disregarded and another pair was prepared and measured. If the mean absorbance of the pair fell outside the control limits for $\bar{x}$, lower concentrations of the interferer were tried until the mean absorbance was within the control limits.

The anions tested were added as sodium or potassium salts and the cations were added as acetates, chlorides, nitrates, or sulfates.

No interference was observed when 25 mg. of the following ions were present: acetate, ammonium, barium, beryllium, borate, bromide, cadmium, calcium, chloride, chromium(III), cobalt, copper(II), iodate, iodide, lithium, magnesium, manganese(II), mercuric, nickel, nitrate, selenium(IV), strontium, and tartrate. The maximum permissible amounts of the ions which were found to interfere are given in Table VI.

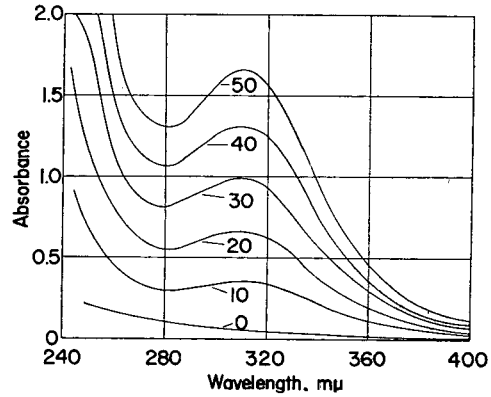


Figure 2. Absorption Spectra of Solutions of Molybdophosphoric Acid

Prepared according to recommended general method. Number of micrograms of phosphorus present shown on each curve. Measurements made with Cary spectrophotometer using 1-cm. cells, 0.1-mμ band width, and solvent in reference cell

Recommended General Method. On the basis of the foregoing experimental work, a recommended general procedure was designed.

APPARATUS. The absorptiometer should be capable of making absorbance measurements at 310 mμ.

REAGENTS. Mixed Reagent Solution. Dissolve 7.5 grams of reagent grade sodium molybdate dihydrate in 200 ml. of water, add 100 ml. of reagent grade hydrochloric acid, specific gravity

Table VI. Interfering Ions

(Each sample contained 25γ of phosphorus and was carried through recommended general method)

Ion	Added	Max. Permissible Amt. for Adherence to Control Limits, Mg.
Al^{+++}	$Al(NO_3)_3$	12.5
As^{+++++}	H_3AsO_4	4
Au^{+++}	$AuCl_3$	0
Bi^{+++}	$BiCl_3$	0
Citrate	$Na_3C_6H_5O_7$	5
$Cr_2O_7^{--}$	$K_2Cr_2O_7$	0
Fe^{+++}	$FeCl_3$	10
F^-	NaF	1
Formate	$NaCHO_2$	10
Ge^{++++}	Na_2GeO_3	1
Pb^{++}	$Pb(C_2H_3O_2)_2$	0
NO_2^-	$NaNO_2$	0
IO_4^-	KIO_4	1
MnO_4^-	$KMnO_4$	1
Si^{++++}	Na_2SiO_3	5
SCN^-	KSCN	0
$S_2O_3^{--}$	$Na_2S_2O_3$	0
Th^{++++}	$Th(NO_3)_4$	0
WO_4^{--}	Na_2WO_4	10
UO_2^{++}	$UO_2(NO_3)_2$	0
VO_3^-	$NaVO_3$	1
Zn^{++}	$ZnCl_2$	1
ZrO^{++}	$ZrO(NO_3)_2$	0

1.19, and dilute to 500 ml. Store in a hard-rubber or polyethylene bottle.

Standard Phosphorus Solution. Dissolve 0.1098 gram of reagent grade, oven-dried potassium dihydrogen phosphate in 1000 ml. of water. Store in a hard-rubber or polyethylene bottle. This solution contains 25γ of phosphorus per ml.

Extractant. Mix 100 ml. of 1-butanol with 400 ml. of chloroform.

CALIBRATION CURVE. Measure out 0, 0.5, 1.0, 1.5, and 2.0 ml. of the standard phosphorus solution and treat and measure according to the procedure below. Construct a graph of absorbance at 310 mμ *vs.* amount of phosphorus.

PROCEDURE. Select a representative sample containing up to 50γ of phosphorus. Treat it in any way necessary, so that the phosphorus is present as orthophosphate in 15 ml. of water whose pH is between 5 and 9 and the concentrations of other ions are below the maximum permissible values of Table VI.

With a pipet, measure 10 ml. of mixed reagent solution and add it to the sample. Pour the resulting solution into a 125-ml. separatory funnel and add 10 ml. of extractant, using the extractant to rinse out the vessel which contained the sample solution. Shake the funnel for 60 seconds, allow the layers to separate, and drain the lower layer into a 25-ml. volumetric flask. Add 10 ml. more of extractant to the separatory funnel, repeat the shaking for 60 seconds, and drain the lower layer into the volumetric flask. Dilute to the mark with extractant.

Measure the absorbance at 310 mμ in a 1-cm. cell with extractant in the reference cell. Refer to the calibration curve to find the amount of phosphorus present.

Determination of Phosphorus in Steel. The sensitivity previously determined is such that up to 50γ of phosphorus can be measured. As phosphorus usually occurs in steel in concentrations of less than 0.1%, 50-mg. samples can be used.

ACIDITY. To avoid loss of phosphorus as phosphine during dissolution of the sample, an oxidizing acid must be used (*19*). It was known from the previous study of acidity that nitric acid can be used satisfactorily, and that the acidity of the solution which is subjected to extraction must be carefully controlled. To achieve the optimum acidity in the final aqueous solution there must be 24 meq. of acid present. The dissolution of 50 mg. of steel will use up 2.5 meq. of acid, so 26.5 meq. are required altogether. If nitric acid, specific gravity 1.42, is diluted to one third its original strength, 5.0 ml. of the diluted solution will supply just the right amount of acid. This strength of acid is recommended for the dissolution of plain carbon steels (*19*).

From 1 to 4 minutes of boiling is satisfactory for removal of nitrogen oxides.

OXIDATION OF CARBON. After dissolution of the sample and removal of oxides of nitrogen, 10 ml. of a 2% solution of ammonium peroxydisulfate was added to oxidize carbon. From 1 to 4 minutes of boiling is satisfactory for destruction of excess peroxydisulfate. If the excess is not destroyed, permolybdic acid is formed and low results are obtained.

MOLYBDATE CONCENTRATION. The use of 10 ml. of 1.5% solution of sodium molybdate dihydrate was continued.

INTERFERENCE BY IRON. Reference to Table VI shows that no more than 10 mg. of iron may be present without causing interference. This is overcome by having the iron present as ferric nitrate instead of ferric chloride, as it was when testing interferences. A calibration curve prepared from samples each of which contained 50 mg. of iron as ferric nitrate was superimposed on a calibration curve made with no iron present.

Recommended Method for Determining Phosphorus in Steel. The following apparatus and reagents are needed:

APPARATUS. The absorptiometer should be capable of making absorbance measurements at 310 mμ.

REAGENTS. Nitric Acid. Dilute 100 ml. of reagent grade acid, specific gravity 1.42, to 300 ml.

Ammonium Peroxydisulfate Solution. Dissolve 2 grams of reagent grade ammonium peroxydisulfate in 100 ml. of water. Prepare fresh daily.

Sodium Molybdate Solution. Dissolve 1.5 grams of sodium molybdate dihydrate in 100 ml. of water. Store in a hard-rubber or polyethylene bottle.

Table VII. Determination of Phosphorus in NBS Steel Samples

Type of Steel	NBS No.	Certificate Value, % P	P Found[a] %
BOH	11d	0.006	0.006
BOH	12d	0.013	0.014
BOH	13c	0.013	0.015
BOH	14c	0.012	0.013
BOH	15a	0.007	0.008
BOH	16c	0.032	0.034
AOH	19d	0.033	0.035
AOH	20c	0.044	0.042
AOH	21a	0.063	0.063
AOH	21c	0.062	0.062
AOH	34	0.095	0.096
AOH	34a	0.028	0.029
AOH	35	0.033	0.032
Bessemer	8d	0.099	0.098
Bessemer	22b	0.084	0.082
Bessemer	23a	0.102	0.103
Elec.	51	0.011	0.009
Basic elec.	65b	0.031	0.031
Mn rail	100	0.023	0.022
Cr-V	30a	0.020	0.019
Ni	33b	0.037	0.037
Ni-Cr	32b	0.016	0.014
Cr-Mo	72	0.016	0.017

[a] Average of 2 determinations differing by 0.003% P or less.

Extractant. Mix 100 ml. of 1-butanol and 400 ml. of chloroform.

Standard Phosphorus Solution. Dissolve 0.1098 gram of reagent grade, oven-dried potassium dihydrogen phosphate in 1000 ml. of water. Store in a hard-rubber or polyethylene bottle. This solution contains 25γ of phosphorus per ml.

CALIBRATION CURVE. Measure 0, 0.5, 1.0, 1.5, and 2.0 ml. of the standard phosphorus solution and add 4.5 ml. of nitric acid. (This differs from the amount used on the sample because of allowance for the acid used up in dissolving the sample.) Dilute each solution to 15 ml. and add 10.0 ml. of sodium molybdate solution. Extract and measure according to the procedure given below. Plot a graph of absorbance at 310 mμ *vs.* amount of phosphorus.

PROCEDURE. Select a representative sample of a steel which will dissolve in 5 *N* nitric acid. If the phosphorus content is less than 0.1%, weigh a sample of approximately 50 mg. If the phosphorus content is higher, weigh a correspondingly smaller sample. Place the sample in a 50-ml. conical flask and add a boiling chip. Add 5.0 ml. of nitric acid and let stand until all action ceases.

Boil the solution for 2 minutes, add 10 ml. of ammonium peroxydisulfate, and boil 2 minutes more. Let cool to room temperature and add 10.0 ml. of sodium molybdate solution.

Transfer the solution to a 125-ml. separatory funnel and add 10 ml. of extractant, using the extractant to rinse the conical flask. Shake the separatory funnel for 60 seconds and let the layers separate. Drain the extractant (lower layer) into a 25-ml. volumetric flask and repeat the extraction. Add the second portion of extractant to the first and dilute to the mark with extractant.

Measure the absorbance at 310 mμ in a 1-cm. cell using extractant in the reference beam. Refer to the calibration curve to find the amount of phosphorus in the sample.

ANALYSIS OF STANDARD SAMPLES

The procedure was tested by analyzing some plain and low-alloy steels supplied by the National Bureau of Standards. The averages of duplicate determinations are shown in Table VII.

CONCLUSIONS

A procedure is recommended which enables one to measure 25 micrograms of phosphorus in the presence of 4 mg. of arsenic, 5 mg. of silicon, or 1 mg. of germanium. The concentrations of reagents were found to be critical and the reagent solutions must be measured with pipets.

The molar absorptivity for phosphorus is 24,400 liters per mole-cm. by this procedure. This is almost as sensitive as the heteropoly blue procedure of Boltz and Mellon, which has a molar absorptivity of 26,800 liters per mole-cm. at 830 mμ (*5*). The molar absorptivity of the molybdovanadophosphoric acid method of Kitson and Mellon is 558 liters per mole-cm. at 460 mμ (*17*).

Steels containing up to 0.1% phosphorus were successfully analyzed in the presence of as much as 1.4% manganese, 0.3% silicon, 1.0% chromium, or 0.2% vanadium.

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Determination of Trace Elements in Fuel Oils

Direct Spectrographic Method

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This spectrographic method was developed to provide a rapid and accurate means of determining the concentration of vanadium, sodium, nickel, and calcium in residual fuel oils without prior ashing. Because of the adverse effects which certain combinations of these elements may have during combustion in high temperature boilers or gas turbines, it is essential that the manufacturing processes be controlled by precise analyses. Conventional wet-chemical or spectrographic methods performed on the ash of such fuels are very time-consuming and are subject to loss or contamination errors during the ashing phase. A rotating disk electrode composed of graphite and lithium carbonate introduces a solution of fuel oil, internal standard, and buffer into a high voltage spark discharge. During the discharge, an inert atmosphere is maintained in the arc-spark stand. By using Type 103-F film, and positioning the spectrographic camera, a single exposure covers a spectral range of 3265 to 5915 A. on a 25-inch strip of film. Standards are prepared by adding metal salts of 2-ethyl hexoic or oleic acid to a fuel oil of known composition. Line pairs of the elements and internal standard were chosen to provide good reproducibility and sensitivity. A single sample may be analyzed in 40 minutes, as compared to approximately 16 hours by chemical methods. More frequent analyses by this method provide better control over processing, transportation, storage, and utilization of residual fuel oils.

KNOWLEDGE of the type and amounts of metallic elements that may be deposited during the combustion of residual fuel oils is often essential to the successful utilization of this source of energy. In some concentrations the metals in fuel oils may collect as ashes on furnace tubes or in gas turbines and cause serious deposits or corrosion.

Vanadium, sodium, and sulfur are the major constituents commonly found in fuel oil ashes which have a pronounced effect on collecting of deposits or corrosion. Nickel, iron, chromium, magnesium, and barium are of secondary importance. Naturally occurring or added calcium in optimum amounts may reduce or entirely eliminate the deleterious effects of the other metals. These elements may be present in crudes as metal-organic compounds or as inorganic salts and they generally tend to concentrate in the heavier portions during fractionation and processing. The concentration of each will vary with the source of oil, but in all cases their total concentration is low. Even the heaviest grade of normal Bunker C fuel contains a maximum of 0.1% ash (*1*). Generally, it is considerably below this amount; however, when combustion improvers or additives have been included, this amount may be substantially increased. Sulfur may be present in the elemental form or it may be combined in an organic or inorganic matrix.

Vanadium in the ash of fuel oils is generally present as vanadium pentoxide and sodium as sodium sulfate, with lesser amounts of sodium-vanadate complexes (*5*). Because of the critical dam-

age that may result from such ashes in certain combinations, it is essential that those present in major concentrations be known. In the authors' laboratory a knowledge of the concentration of vanadium, sodium, nickel, and calcium in Bunker C fuel oil was required. Conventional dry-ashing techniques are subject to losses or to contamination during combustion. Wet-ashing techniques are prone to give erroneous results because of contamination from the reagents or containers used. Any ashing procedure followed by chemical or spectrographic analysis is very time-consuming. It was evident that the greatest saving in time would result from eliminating ashing and introducing the sample directly into the electrical discharge with little or no prior sample preparation. Furthermore, this would eliminate losses or errors that might result during this part of the analysis. For these reasons, investigative work toward developing a direct spectrographic method of analysis for trace elements in fuel oils was undertaken.

INVESTIGATION

A rotating disk electrode has been used by the authors for nonmetallic matrices, such as cracking catalysts (*3*), and for hydrocarbon matrices of gas oil, lubricating oil, and greases. Other authors have reported this same usage (*4*). Consequently, it was believed to offer the best solution for this problem. Studies indicated that with a rotating disk electrode introducing the fuel oil with its metallic constituents into a high voltage discharge in an inert atmosphere, vanadium, nickel, and calcium lines of adequate sensitivity were available in the ultraviolet spectral range. However, no sodium lines with sufficient sensitivity were found in this region. This difficulty was overcome by using Eastman Type 103-F film in the ARL 2-meter spectrograph and positioning the camera to cover the 3265 to 5915 A. range in a single exposure.

Table I. Sensitivity Enhancement by Buffers

	Graphite Only		Graphite plus Li_2CO_3	
	Fuel oil only	Fuel oil with Ba[a]	Fuel oil only	Fuel oil with Ba[a]
	Intensity Ratios, $\frac{I\ Element\ Line}{I\ Background}$, Av. of 4 Values			
Element				
Ba	...	2.4	..	5.1
Ca	1.3	3.2	7.9	9.3
Na	7.5	[b]	24.0	[b]
Ni	3.5	4.3	3.9	4.4
V	2.0	3.0	5.5	5.9

[a] Barium 2-ethyl hexoate.
[b] Barium compound contained sodium as an impurity; therefore, sodium ratios were not determined in these instances.

This encompasses reasonably sensitive lines for the elements sought. Further improvements in sensitivity for some of the elements were obtained by incorporating lithium carbonate into the disk and by using barium 2-ethyl hexoate as a buffer. These improvements are shown in Table I, where an increase in ratio of line to background intensity denotes a comparable increase in sensitivity. The improvement in reproducibility derived from the barium buffer is shown in Table II. These data are average results obtained from 50 analyses of the fuel alone and 25 analyses of the fuel plus the barium 2-ethyl hexoate. More desirable working curves were obtained when the barium buffer was used. Disk composition was established at 1 part of lithium carbonate to 4 parts of S.P. 1 graphite and the briquetting pressure at 100,000 pounds per square inch. The effect of disk weight on reproducibility is shown in Table III, which indicates that a 1.3-gram disk offers the best compromise. This quantity of graphite and lithium carbonate in a mold 0.5 inch in diameter produces a disk approximately $^3/_{16}$ inch thick; however, the weight of the disk is the critical measurement.

Table II. Reproducibility Improvement by Barium Buffer

Element	Fuel Oil Only (50 Determinations)	Fuel Oil plus Ba 2-Ethyl Hexoate (25 Determinations)
Ca		
Av. deviation, %	11	4.4
Range, %	54	21
Na		
Av. deviation, %	18	6.4
Range, %	120	23
Ni		
Av. deviation, %	12	3.0
Range, %	70	14
V		
Av. deviation, %	5.7	3.4
Range, %	50	15

The arc-spark stand on the spectrograph used for this work was modified to permit the introduction of nitrogen into the electrode housing. An inert atmosphere was found necessary to prevent ignition of the fuel oil during the discharge. It also increased the sensitivity. The nitrogen was admitted into the arc-spark stand through a $^1/_4$-inch copper tube in the base and another from the side nearest the spectrograph just above the optical axis. The exit end of the base tube was compressed to prevent the flow of nitrogen from this point. Its walls were perforated by approximately 12 $^1/_{16}$-inch holes distributed over the surface. The tube above the optical axis had an open end and was adjusted to direct the flow of nitrogen into the discharge zone. A suction tube was inserted through a hole in the observation glass opposite the spectrograph and in line with the nitrogen inlet tube, thereby providing a means of removing any vapors as soon as they were formed. The nitrogen flow into the arc-spark stand was controlled by a pressure regulator in conjunction with flowmeters, 0.7 cubic foot per minute entering along the axis and 1 from the base.

EQUIPMENT

The Applied Research Laboratories 2-meter spectrograph, with the camera positioned to cover the 3265° to 5915° F. range on a 25-inch strip of 103-F spectral film, is used for this work. The prespark and exposure times are controlled automatically.

An ARL Precision source unit with a high voltage spark case is utilized.

A three-tray, ARL film-developing machine, thermostatically maintained at 65° F., is used to process the film, which is dried in a film-drying machine.

Table III. Effect of Disk Weight on Reproducibility

	Disk Weight, Grams		
	1.1	1.2	1.3
	Intensity Ratios, $\frac{I\ Element\ Line}{I\ Cobalt\ Line}$, Av. of 5 Values		
Element			
Ca			
Av. deviation, %	4.3	5.0	1.8
Max. deviation, %	10	7.8	4.1
Na			
Av. deviation, %	6.0	7.2	2.4
Max. deviation, %	8.0	10.	4.0
Ni			
Av. deviation, %	3.9	1.7	2.0
Max. deviation, %	8.7	3.2	2.2
V			
Av. deviation, %	4.2	1.3	3.1
Max. deviation, %	9.7	3.1	6.2

The spectrograms are read on an ARL projection comparator densitometer.

A specimen briquetting press, with a mold $^1/_2$-inch in internal diameter equipped with a pin to produce a $^1/_8$-inch hole in the center, is used to compress the disk electrodes.

A Dunn-Lowry calculator is used for the calculations.

No. 6A porcelain boats with a notch cut in the right side, approximately 1.75 inches from the handle end, are used to hold the sample during discharge.

Auxiliary equipment, such as mechanical stirrers, a hot plate, an analytical balance, general analytical laboratory facilities, bottled nitrogen, pressure regulator, and flowmeters are required.

STANDARDS, INTERNAL STANDARD, AND BUFFER

The standards were prepared by adding to a fuel oil of known composition vanadium oleate and the nickel sodium and calcium salts of 2-ethyl hexoic acid dissolved in a refined naphtha. The vanadium was a commercial preparation diluted to the required concentration. The hexoates, which were prepared in the authors' laboratory, contained a 100% excess of 2-ethyl hexoic acid to ensure their solubility in the heavy naphtha. This naphtha, which was predominantly paraffinic-type hydrocarbons with a boiling range of approximately 355° to 385° F., was used to reduce the viscosity of the hexoates sufficiently to permit satisfactory handling and to assure uniform distribution throughout the fuel oil. Aliquots of these solutions were blended with a residual fuel oil to give known concentrations of the four metals. The base fuel had been previously analyzed by spectrographic addition procedures, whereas the naphtha solutions of the metallic salts were analyzed chemically.

Table IV. Discharge and Exposure Conditions

High precision case	
Capacity, microfarad	0.007
Inductance, microhenrys	360
Current, amperes	8.5
Intensity control stand position	1/5
% Transmittance	100
Grating shutter setting	0.3
Prespark, seconds	48
Exposure, seconds	12
Disk, r.p.m.	14

The barium salt, used as the buffer, was prepared from 2-ethyl hexoic acid and barium hydroxide. Cobalt, the internal standard, was also introduced as 2-ethyl hexoate, which was prepared by a double decomposition reaction between lithium 2-ethyl hexoate and cobalt nitrate. Again, as in the preparation of the standards, a 100% excess of the 2-ethyl hexoic acid was necessary to ensure complete solubility in the hydrocarbons. Both the barium and cobalt hexoates were simultaneously dissolved in the paraffinic-type naphtha used to add metal salts to the fuel oil standards. The finished solution contained 120 mg. of barium and 1.5 mg. of cobalt per gram of solution.

In order to obtain standards and an internal standard-buffer solution with an unobjectionable sodium concentration, the following precautions were taken.

Prior to its use, all glassware was meticulously cleaned with an acid cleaning solution, followed by multiple rinses with demineralized water of approximately 1,000,000 ohms per cc. resistance. Water of this purity was used wherever needed. Reactions involving the production of the hexoates were carried out in Vycor vessels. When borosilicate glass containers were used for this purpose, the sodium concentration was excessively high. All reagents were analyzed for sodium and only those which contributed less than 0.5 p.p.m. to the total amount of this element in an analysis were acceptable. The sodium was removed from the hexoic acid by vacuum distillation. The naphtha diluent was washed with dilute hydrochloric acid, followed by water washing. Polyethylene bottles were used to store prepared solutions wherever practical. These efforts reduced the sodium contribution of most preparations to an undetectable amount at the concentrations used in an analysis. The buffer–internal standard solution contributed approximately 0.5 p.p.m. of the total sodium in an analysis; however, a correction is made for this amount.

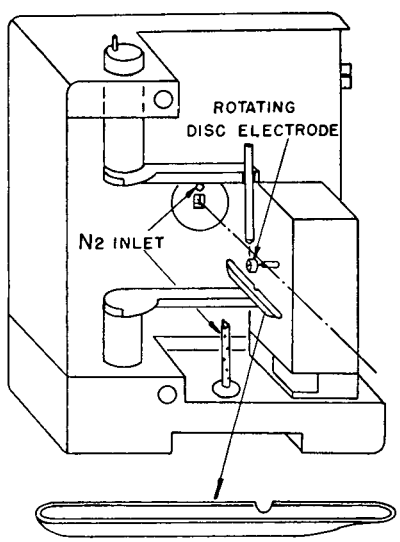


Figure 1. Arc-Spark Stand Assembly

PROCEDURE

The fuel oil sample to be analyzed is thoroughly mixed in its original container, by heating the sample in an oven until its temperature is between 150° and 175° F., then thoroughly agitating it with a mechanical stirrer having a glass or stainless steel shaft and propeller. Unless the oil is known to be dry, a portion

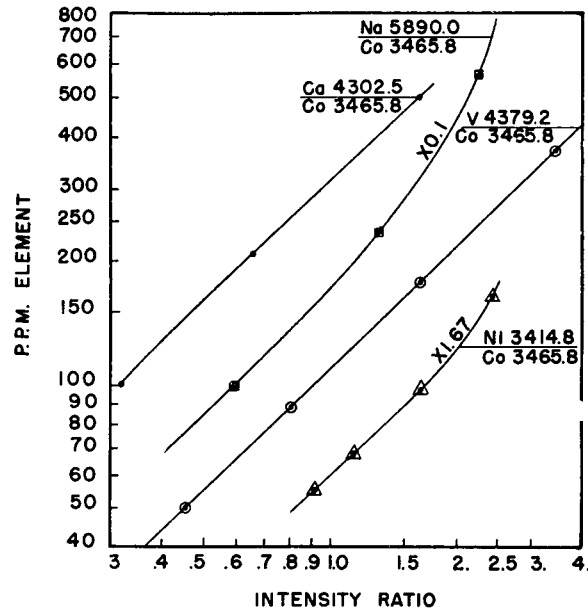


Figure 2. Working Curves for Direct Fuel Oil Method

Barium buffer

of about 25 grams is dehydrated by heating with absolute alcohol. Sixteen grams of this sample is then weighed into a tared, 100-ml. Berzelius beaker. To this is added 4.92 grams of the naphtha solution containing barium and cobalt 2-ethyl hexoates. For ease in weighing, this solution is usually added by means of a pipet. Complete homogeneity is assured by using a mechanical stirrer to blend the sample thoroughly while it is being warmed on a hot plate.

Table V. Approximate Lower Limits of Detectability

(Direct fuel oil method)

Element of Line	Lower Limit, P.P.M.
Ca 4226.7	0.4
Na 5890.0	0.2
Ni 3619.4	10
V 3184.0	2

A No. 6A porcelain boat is filled to the bottom of the notch with the blended sample–internal standard–buffer mixture. The boat is positioned in the arc-spark stand, so that the stainless steel shaft which holds the rotating disk fits into the groove without binding. Figure 1 shows the arc-spark stand assembly; however, for the sake of clarity in the sketch, the boat has been lowered and the door, with its suction tube, has been removed. The counterelectrode is a $\frac{1}{4}$-inch spectrographic carbon rod with a 120° cone and is gapped at 3 mm. Prior to the discharge the door is closed, the vacuum system started, and the flow of nitrogen regulated. Discharge and exposure conditions shown in Table IV are used.

Table VI. Analyses of Sample of Bunker C Fuel Oil

	Spectrographic				Chemical							
					Laboratory A				Laboratory B			
	Ca	Na	Ni	V	Ca	Na	Ni	V	Ca	Na	Ni	V
No. of analyses	9	9	9	9	10	9	10	13	8	8	8	10
Element, p.p.m., av.	317	12.0	96	51	302	15.2	89	50.8	288	14.0	74	57
Range, p.p.m.	290–340	10.7–13.5	91–102	48–54	287–316	13.2–17.6	85–92	48–53	285–292	12.7–15.0	72–78	53–59
Std. dev., p.p.m. of sample	16.9	0.88	3.16	1.94	8.05	1.38	2.26	1.39	2.67	1.13	2.24	1.7
Std. dev., % of element	5.3	7.3	3.3	3.8	2.7	9.1	2.5	2.7	1.6	8.1	3.0	3.0
Range, % of element	16	23	11	12	9.6	29	7.9	9.8	2.4	16	8.1	10.5

FILM DEVELOPMENT

The Eastman Type 103-F film is developed for 2 minutes in Eastman D-8 developer with constant agitation. The temperature of the developing trays is maintained at 65° F. The film remains in the short-stop solution for 0.5 minute and in the Kodak Liquid X-Ray fixer for 2 minutes. It is washed for 5 minutes in a washing tray. Drying is accomplished in 4 minutes in the ARL dryer.

WORKING CURVES AND CALCULATIONS

Exposure conditions for residual fuel oils with an ash content ranging between 100 and 1500 p.p.m. are adjusted to give a negligible background; consequently, this is ignored during subsequent densitometry.

Working curves were prepared from the ratios of line pair intensity *vs.* parts per million concentration, using logarithmic coordinates. Typical curves for the fuel oils mentioned above are shown in Figure 2.

Fuel oils which have an ash content below 100 p.p.m. are rarely analyzed in the authors' laboratory. For such oils different line pairs with greater sensitivity are used and temporary working curves are drawn. Discharge and exposure conditions shown in Table IV are used, except that the background transmittance is adjusted to give approximately 80% of clear film transmittance, by changing the grating shutter setting to 1.0. The lower limits of detectability for this method, shown in Table V, apply to the most sensitive, usable lines for the elements concerned from 2400° to 5930 A. In the densitometry the background transmittance is read and a correction is made for it in the calculations.

The calculations for fuel oils with a normal ash content are made on the Dunn-Lowry calculator. Those for fuels of very low ash content are made from the temporary working curves. Use of the Dunn-Lowry calculator considerably reduces the time required for routine calculations.

DISCUSSION

The chemical determination of the metallic constituents of a residual fuel oil must be made on the ash after all the carbonaceous portion has been completely oxidized. Allowing approximately 8 hours for ashing and a minimum of 8 hours for analyses, the time required for the determination of the vanadium, sodium, nickel, and calcium in a single sample is approximately 16 hours. A comparable analysis may be made by the spectrograph in approximately 10 hours, including ashing. When a combined ashing microtechnique and spectrographic method is utilized, the total time may be reduced to approximately 3 hours. However, the time required to ash the sample and the potential errors inherent in ashing techniques make these methods undesirable for routine applications.

The direct spectrographic method described requires 40 minutes for the analysis of a single sample. This time may be further reduced by grouping and analyzing several samples simultaneously. The rapidity with which such analyses may be made greatly facilitates the processing or blending of fuel oils to meet specifications covering their metallic constituents.

Shown in Table VI is a comparison of results obtained on a sample of Bunker C fuel oil by this spectrographic procedure and chemical methods by two laboratories. All results listed under "Chemical" are based upon ashing, with subsequent analyses of the ash. Included among the procedures are gravimetric, titrametric, colorimetric, polarographic, and flame photometric methods. The chemical methods, or modifications thereof, which were used by Laboratory A are as follows:

1. Sodium was determined gravimetrically by weighing a precipitate of sodium uranyl acetate (*7*).
2. Vanadium was determined colorimetrically by measuring the spectrophotometric absorption of a phosphotungstovanadate solution (*2*).
3. Nickel was determined colorimetrically, following the procedure reported by Wrightson (*8*).
4. Calcium was determined by precipitation as the oxalate and titrating with permanganate (*6*).

The spectrographic method has also been used to determine sodium, vanadium, nickel, and calcium in crude oils, in the same manner as with fuel oils after the gasoline fraction had been removed by a laboratory distillation. The metals were concentrated in the bottom fraction, which was then blended with the naphtha-buffer–internal standard solution and handled like a residuum fuel oil. The accuracy is comparable to that obtained on the Bunker C type fuel oils.

CONCLUSIONS

A direct spectrographic method for the determination of vanadium, sodium, nickel, and calcium in fuel oils has been developed, which requires 40 minutes for a single determination, compared to several hours or days by spectrographic, chemical, or physical methods based upon the ash. The precision and sensitivity are comparable to those obtained by the longer methods. This method is well suited for routine analyses where processing or blending must be closely controlled.

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Fractionation of Barium-Radium Mixtures as Chromates

By Precipitation from Homogeneous Solution

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Fractional precipitation from homogeneous solution was investigated as a method for the rapid concentration of radium from barium-radium mixtures. When chromates were homogeneously precipitated, radium concentrated in the crystals with a logarithmic type of distribution. Homogeneous precipitation resulted when nitric acid solutions of the chromates were gradually neutralized, using urea or potassium cyanate as an internal reactant to generate ammonia uniformly throughout the solution. Experiments indicated that the separation is improved by decreasing the temperature at which the precipitations are made, but is not affected by the composition (barium-radium ratio) of the original mixture or the concentration of barium in solution. In order to compare the separation obtained by the fractionation of various salts, regardless of the precipitation conditions, a theory is presented based on the determination of limiting distribution coefficients. The separation obtained per fractionation step by the homogeneous chromate procedure was equivalent to that obtained by the fractional crystallization of the bromides and better than that by the fractionation of the chlorides or nitrates.

RADIUM is usually separated from barium by fractional crystallization of a barium-radium chloride or bromide mixture (*1, 3, 8, 15*). The method depends on the fact that a greater percentage of radium than barium crystallizes at each fractionation step. Fractional crystallization is a reliable method and has been used to good advantage in separating this pair of chemically similar elements. However, the separation is laborious and slow, and its operation requires considerable space. As separation procedures involving fractional precipitation are generally more rapid than those using fractional crystallization, numerous investigations (*18*) have been carried out in an attempt to develop suitable fractional precipitation procedures.

This paper deals with the conditions for the concentration of radium by the fractional precipitation of barium-radium chromate mixtures. Chromates were chosen for a series of radium enrichment studies because a survey of the literature (*18*) indicated that chromates gave better separations than any other salt, and because fractional precipitation could be used rather than the more time-consuming fractional crystallization.

RADIUM DISTRIBUTION LAWS

When a radium salt is coprecipitated with a barium salt, there are two systematic ways in which radium may be distributed in the crystals. One type of distribution is expressed by the homogeneous distribution law introduced by Henderson and Kracek (*6*) in which the radium-barium ratio in the precipitated crystals is proportional to the radium-barium ratio in the final solution:

$$\left(\frac{\text{Ra}}{\text{Ba}}\right)_{\text{crystals}} = D\left(\frac{\text{Ra}}{\text{Ba}}\right)_{\text{solution}}$$

where D is the homogeneous distribution coefficient. The distribution law represents a state of true thermodynamic equilibrium in which the solid phase has been digested sufficiently to remove all concentration gradients and is homogeneous.

A second type of radium distribution is characterized by the logarithmic distribution law derived by Doerner and Hoskins (*4*) and is expressed by the following equation:

$$\log \frac{\text{total Ra}}{\text{Ra in solution}} = \lambda \log \frac{\text{total Ba}}{\text{Ba in solution}}$$

where λ is the logarithmic distribution coefficient. In this case a state of true thermodynamic equilibrium should exist at all times with respect to the solution and an infinitesimal surface layer on the crystal (but not with the crystal as a whole, which retains a radial concentration gradient). Accordingly, if the thermodynamic system is restricted to the surface layer of the crystal and to the solution in equilibrium, the two distribution laws become identical. However, as it is difficult to measure the surface concentration accurately, it is customary to analyze the crystal as a whole. Thus the simple distribution must be integrated over the period of crystal growth which results in the logarithmic relationship. Bonner and Kahn (*2*) reviewed the literature and described the types of distribution obtained under various precipitation conditions when a radium salt is coprecipitated with a barium salt.

For a given set of ideal conditions which lead to homogeneous distribution, the calculated values of D remain constant while the values of λ decrease as the amount of barium salt precipitated increases. Conversely, for a set of ideal conditions which lead to logarithmic distribution, the values of λ remain constant while the values of D increase as the amount of barium salt precipitated increases. The value obtained for D under the conditions which lead to homogeneous distribution, theoretically, should equal the value of λ under the conditions which lead to logarithmic distribution.

Since it is difficult to maintain experimental conditions which exclusively favor one type of distribution, the distribution laws do not adequately describe the major portion of the work that has been done on the distribution of radium in barium salts. Generally, neither D nor λ is constant, but each shows a trend with the fraction of barium salt crystallized or precipitated (*9*). Nevertheless, the distribution theories are helpful in selecting a practical method for the separation of barium and radium. Distribution coefficients greater than unity represent radium enrichment in the precipitate, while those less than unity represent enrichment in the filtrate. The salt selected for a separation of barium and radium should be one which shows extreme values of D and λ. If the separations are to be as efficient as possible, methods leading to the logarithmic type of distribution should be employed (*2*). For example, if the value of the distribution coefficient is 10, precipitation of 50% of the barium removes 99.8% of the radium if the radium is logarithmically incorporated in the crystals, but only 90.9% if it is homogeneously incorporated.

HOMOGENEOUS PRECIPITATION

In the procedures used by Henderson and Kracek (*6*) and by Nikitin (*14*) for the fractional precipitation of barium-radium mixtures, rapid precipitation of the chromates was made by the addition of a precipitating reagent. In this type of precipitation, which is often called heterogeneous precipitation (*5*), the degree

of local supersaturation caused by the addition of the precipitating reagent is so erratic that a somewhat random distribution of radium is obtained.

In the fractionation procedure described in this paper the chromates are precipitated in a manner which approaches about as closely as possible the ideal conditions for the logarithmic type of distribution with its added increase in efficiency. The procedure is frequently referred to as precipitation from homogeneous solution (*5, 23*). It can be controlled simply, provides uniform results, and is rapidly carried out. The procedure depends upon the decrease in solubility of the chromates with decreasing acid concentration. By gradual neutralization the solution becomes slightly supersaturated and, thus, the radium and barium chromates precipitate. To fulfill the requirements of a homogeneous aqueous phase (required for thermodynamic equilibrium), the neutralizing base (ammonia) is generated uniformly throughout the solution by spontaneous hydrolysis of a previously added reagent, urea (*24*) or potassium cyanate (*17*).

The mechanism for the hydrolysis of urea was reported by Warner (*22*):

$$CO(NH_2)_2 \rightleftharpoons NH_4^+ + OCN^-$$

$$OCN^- + H_3O^+ \rightarrow NH_3 + CO_2$$

From examination of the above reactions it is obvious that either urea or a cyanate will hydrolyze to produce ammonia. Boiling solutions are required for the isomeric conversion of urea to ammonium cyanate in the first step of the hydrolysis. By using a cyanate instead of urea, it is possible to precipitate the chromates at any temperature between the freezing and boiling points of the solution. The temperature at which the precipitation is made can be significant. Merkulova (*12*) reports that the radium distribution coefficients, D, obtained from fractional recrystallization studies increase with decreasing temperature.

Three variables were studied to determine their effects on the distribution coefficients obtained by fractional chromate precipitation from homogeneous solution: radium concentration in the original barium-radium mixture, barium concentration in solution, and temperature.

RADIUM CONCENTRATION STUDIES

The radium concentration with respect to barium was varied over a wide composition range by using a simple batch fractionation system (*11, 19*) in which 50% of the barium was precipitated in each fractionation step. The temperature at which the precipitations were made was 100° C.

One hundred grams of a barium-radium carbonate mixture (Ba:Ra = 96,930:1) was moistened with 250 ml. of water and dissolved by slowly adding 100 ml. of concentrated nitric acid. After dilution with water to 3 liters, the nitrate solution was heated to 95° C. Fifty grams of potassium chromate, dissolved in 200 ml. of hot, dilute nitric acid (1 to 3), and 192 grams of urea were added to the solution. The reaction mixture was maintained at 100° C. until sufficient urea hydrolyzed to raise the pH to 5. Barium-radium chromate precipitated and was filtered.

The radium-enriched precipitate, which contained about half the original quantity of barium, was dissolved in 800 ml. of hot 1 N nitric acid. The solution was diluted with 2.4 liters of hot water. After the addition of 192 grams of urea, the temperature was maintained at 100° C. for 42 minutes. A second fraction of barium-radium chromate precipitated. The precipitation was stopped by the addition of a few milliliters of cold water to cool the solution below 90° C. The precipitate was filtered immediately and used in a third fractionation step.

All subsequent fractionations were carried out in the same manner as the second step, except that in each step the amounts of reagents were reduced to one half of that required in the preceding step. For example, the second barium-radium chromate fraction was dissolved in 400 ml. of 1 N nitric acid. The solution was diluted with 1.2 liters of water, and 96 grams of urea was added. The fourth fractionation step required only 200 ml. of 1 N nitric acid, 600 ml. of water, and 48 grams of urea. The fifth step required half the amounts used in the fourth step, etc.

Table I. Concentration of Radium by Fractional Chromate Precipitation

Fraction	Barium, G.	Radium, Mg.	Distribution Coefficient, λ	Ba:Ra Ratio
Original	67.92	0.7007	...	96,930:1
1	35.62	0.6715	4.28	53,050:1
2	17.07	0.6356	4.49	26,860:1
3	8.72	0.6088	4.43	14,320:1
4	4.72	0.5898	4.45	8,003:1
5	2.28	0.5590	4.59	4,079:1
6	1.19	0.5309	4.05	2,241:1
7	0.71	0.5136	3.77	1,382:1
First concentrate	3.467	1.680	...	2,064:1
8	1.478	1.502	4.04	984:1
9	0.924	1.388	2.63	666:1
10	0.252	1.097	4.91	230:1
11	0.1395	0.928	2.32	150:1
12	0.0863	0.882	3.12	98:1
Second concentrate	0.2418	2.135	...	113:1
13	0.1538	2.035	3.03	75.5:1
14	0.0512	1.735	4.73	29.5:1
15	0.0215	1.669	6.00	12.9:1
16	0.0066	1.522	6.62	4.3:1
17	0.0017	1.209	5.31	1.4:1
18	0.0003	1.176	18.57(?)	0.26:1
Final concentrate	0.00021	1.172	4.73	0.18:1

Radium was determined in the filtrate from each fractionation step by the method of Tompkins and coworkers (*20*), and the radium in the precipitate was obtained by difference. Barium was determined by drying and weighing the precipitated chromates.

The fraction of barium precipitated in each fractionation step (except the first) depended on a timed reaction, based upon the rate of hydrolysis of urea in hot solution. If the reaction mixture is maintained at 100° C. for 42 minutes, approximately 50% of the barium chromate precipitates. For each minute over 42 minutes an additional 3% of the barium chromate is precipitated; therefore, time control is critical.

Because of the rapid changes in fraction sizes, individual samples could be fractionated only six or seven times before becoming very small. A sample of sufficient size to continue the separation process was obtained by mixing fraction 7 from several fractionation series. This sample, called the "first concentrate" in Table I, contained 3467 mg. of barium and 1.680 mg. of radium (Ba:Ra = 2064:1). In a similar way, a "second concentrate" containing 241.8 mg. of barium and 2.135 mg. of radium (Ba:Ra = 113:1) was prepared by mixing fraction 12 from several series.

BARIUM CONCENTRATION STUDIES

Concentrations of 5, 10, 20, and 30 grams of barium per liter of solution were studied. The carbonate sample used for these studies had a barium-radium ratio of approximately 100,000 to 1. Since radium was present only as a microcomponent, the weight contributed by it was neglected. In each experiment about 20% of the barium was precipitated.

A weighed sample of the barium-radium carbonate was dissolved in sufficient 1 N nitric acid so that the final solution would have a pH of 1.2. After the addition of 5 ml. of glacial acetic acid, the solution was diluted with water to 500 ml. A quantity of potassium dichromate calculated to precipitate 20% of the barium was dissolved in the solution. Finally, 4 grams of potassium cyanate dissolved in a few milliliters of water was added. Precipitation was complete in about 20 minutes. The mixture was filtered, and the precipitates were analyzed for barium gravimetrically and for radium radiometrically (*20*).

TEMPERATURE STUDIES

Fractional chromate precipitations were made at 100°, 25°, and 0° C. on a sample of fixed composition (Ba:Ra = 100,000:1). At each temperature the percentages of radium carried by the precipitation of various percentages of barium were determined. The fraction of barium precipitated in each experiment was fixed

by the quantity of potassium dichromate added to the original solution. The initial barium concentration in each solution was always 10 grams per liter of solution.

The reaction mixture was prepared by adding 100 ml. of water to 7.4 grams of a barium-radium carbonate mixture (equivalent to 5 grams of barium) and dissolving the carbonate by the addition of 7 ml. of 16 *N* nitric acid. If the experiment was to be carried out at 0° or 25° C., 5 ml. of glacial acetic acid was then added. The solution was diluted to approximately 490 ml., and the desired amount of potassium dichromate was added. Depending upon the temperature at which the precipitation was to be made, either 30 grams of urea or 5 grams of potassium cyanate in 10 ml. of water was added.

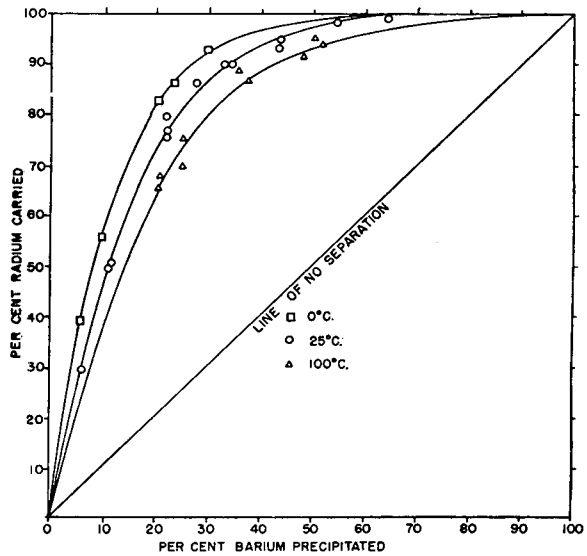


Figure 1. Effect of Temperature on Fractionation of Barium-Radium Chromates

For the reactions carried out at 100° C., urea was used as the internal reactant. (Potassium cyanate was not used because of its uncontrollable, rapid rate of hydrolysis at 100° C.) During the neutralization, the pH of the solution changed from the original value of 1.2 to approximately 6. Since barium chromate is practically insoluble at a pH of 6, the supernatant liquid was nearly colorless. The precipitate was filtered, and the barium-radium mixture remaining in the filtrate was recovered as the carbonate.

For reactions carried out as 25° C. (room temperature) and at 0° C., potassium cyanate was used as the internal reactant. At room temperature precipitation started approximately 3 minutes after the addition of the cyanate and was complete, as evidenced by the color of the supernatant liquid, in about 20 minutes. The procedure at 0° C. required that the reaction mixture be cooled in an ice bath before the addition of the potassium cyanate. The precipitation was complete in about 2 hours.

In all experiments barium and radium were determined in both the solid and liquid phases. The fraction of barium in each phase was determined gravimetrically. Radium was determined by the alpha-counting method (*20*).

The acetic acid acted as a buffer for the reaction in order to prevent the precipitation of barium and radium carbonates which have a reverse order of solubilities compared to the chromates—i.e., radium carbonate is more soluble than barium carbonate (*10*) The acetic acid buffer was not required for the precipitations made at 100° C., as the carbon dioxide was removed by boiling the solutions.

The coprecipitation of a small quantity of nitrates was observed at 0° and 25° C. Qualitative tests applied to many separate washes of the chromate precipitates with hot water indicated the presence of both barium and nitrate ions. The radium enrichment was not improved by washing the precipitates, as proportionate quantities of radium were also removed from the crystals. The coprecipitation of barium nitrate with barium chromate was not observed in precipitations at 100° C.

RESULTS AND DISCUSSION

The concentration of radium by fractional chromate precipitation is shown in Table I. In 19 fractionation steps the composition of the sample changed from an original barium-radium ratio of 96,930 to 1 to a final ratio of 0.18 to 1. The logarithmic distribution coefficient, λ, for each step was calculated from the results of the barium and radium determinations in the various fractions. Although the radium concentration with respect to barium was varied over a very wide composition range, the radium distribution coefficients remained relatively constant. No explanation can be given for the anomalous value obtained for fraction 18, except that it was probably due to analytical errors.

The percentage of radium in the "final concentrate" (84.8% radium) is only slightly below that of commercial-grade radium. The radium chromate was a bright yellow salt resembling barium chromate. The salt glowed weakly in a darkened room with the characteristic light of radium salts.

Table II shows the effect of barium concentration on the radium distribution coefficient. Although the barium concentration was varied from 5 to 30 grams per liter of solution, the calculated logarithmic distribution coefficients show no particular trend over this composition range. Therefore, it appears that the barium concentration has no effect on the distribution coefficient.

Table II. Effect of Barium Concentration on Distribution Coefficient

Barium Concentration, G./L.	Barium Precipitated, %	Radium Carried, %	Distribution Coefficient, λ
5	21.6	77.2	6.06
5	21.4	78.8	6.45
10	22.1	75.7	5.66
10	21.9	79.6	6.44
20	22.5	76.5	5.69
20	22.8	79.7	6.17
30	22.9	82.7	6.74
30	22.2	79.9	6.40

Table III. Effect of Temperature on Distribution Coefficient

Barium Precipitated, %	Radium Carried, %	Distribution Coefficients D	λ
	Temperature 100° C.		
20.6	65.3	7.25	4.59
20.9	67.9	8.01	4.85
25.2	69.8	6.86	4.12
25.2	75.3	9.05	4.82
35.8	88.6	13.94	4.90
37.3	86.9	11.15	4.35
48.5	91.9	12.05	3.75
50.6	95.2	19.36	4.39
52.4	94.3	15.03	3.86
	Temperature 25° C.		
6.0	29.7	6.62	5.69
11.3	50.3	7.95	5.83
11.7	50.6	7.73	5.78
21.9	79.6	13.91	6.43
22.1	75.7	10.98	5.66
22.2	77.0	11.73	5.86
27.9	86.4	16.42	6.10
33.4	89.8	17.56	5.62
34.1	89.9	17.20	5.50
43.7	95.1	25.01	5.25
43.8	93.2	17.59	4.66
54.5	98.7	63.39	5.51
64.5	99.5	109.5	5.12
	Temperature 0° C.		
5.5	39.4	11.17	8.84
9.8	56.2	11.81	8.00
20.1	83.2	19.69	7.95
23.4	86.6	21.13	7.54
29.8	92.7	29.92	7.40

A graphical comparison of the separation of barium and radium at 100°, 25°, and 0° C. is made in Figure 1. Curves obtained by plotting the percentages of radium and barium precipitated (Table III) are compared with a line which represents no separation. As the displacement of a curve from the "line-of-no-separation" is a measure of the attainable separation by a given procedure, it is obvious that the lower the temperature the greater the separation of barium and radium.

Radium distribution coefficients, D and λ, were calculated using the percentages of barium and radium precipitated and the equations which define the two distribution laws. These distribution coefficients are shown in Table III. It is obvious that the logarithmic distribution law is more applicable than the homogeneous distribution law, as the λ values remain relatively constant while the D values increase rapidly with increasing amounts of barium precipitated.

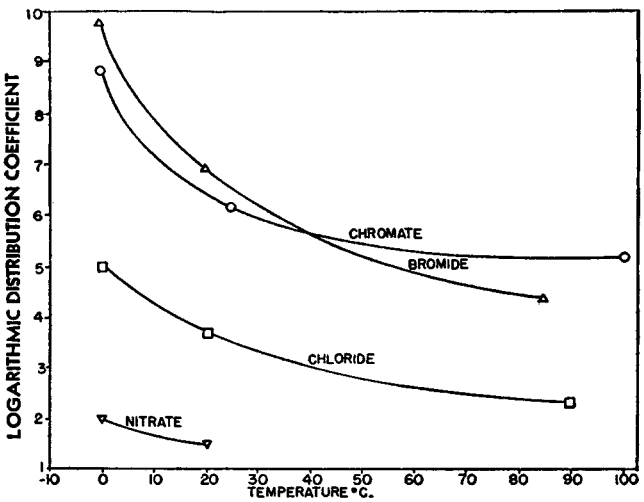


Figure 2. Variation of Distribution Coefficient with Per Cent Barium Precipitated

Actually, a slight deviation from the logarithmic distribution law is observed when the calculated λ values and percentages of barium precipitated are plotted (Figure 2). It is evident that the λ values show a trend toward smaller values when larger fractions of the barium are precipitated. The straight line through each set of points was determined by the method of least squares.

Even though the radium is originally deposited according to the logarithmic distribution law, the increased contact time of crystals and mother liquor in an agitated solution favors the homogeneous distribution of radium. Therefore, a slight decrease in λ is to be expected with increased contact time. This trend is most evident for the experiments made at 0° C., where the crystals of barium chromate were in contact with the mother liquor longer than in the experiments at the higher temperatures.

The logarithmic distribution constants that would be obtained under ideal conditions—i.e., instantaneous precipitation and removal of the crystals from the mother liquor—may be determined from Figure 2 by extrapolating the three lines to 0 % barium precipitated. The authors have designated these extrapolated values as the limiting distribution coefficients. The limiting λ values for the chromate procedures at 0°, 25°, and 100° C. are 8.85, 6.09, and 5.16, respectively. It is significant that the 25° drop in temperature between 25° and 0° C. has a much greater effect on the limiting distribution coefficient than the 75° drop in temperature between 100° and 25° C.

A limiting value for the distribution coefficient represents the distribution of radium between the first infinitesimal amount of salt precipitated and its saturated solution. For any particular

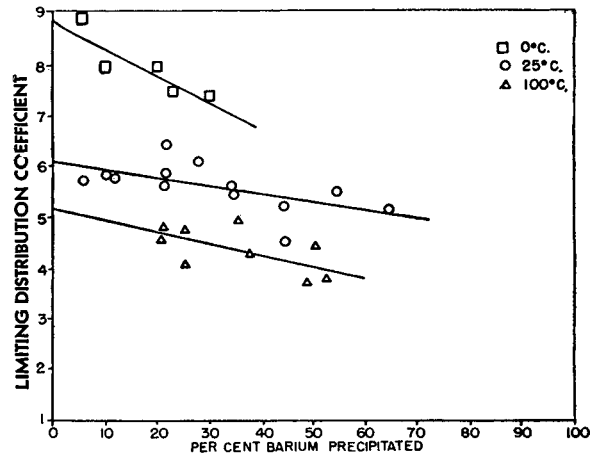


Figure 3. Effect of Temperature on Limiting Distribution Coefficient

fractionation system the limiting values of D and λ are equal. The use of limiting values of the distribution coefficients affords a method of direct comparison of the separation obtained by the fractionation of various salts regardless of precipitation conditions. From data in the literature, limiting distribution coefficients for the fractionation of barium-radium chlorides, bromides, and nitrates were obtained by plotting the percentages of barium

Table IV. Effect of Temperature on Limiting Distribution Coefficients of Several Barium-Radium Salts

Limiting Distribution Coefficient	Fractionation Conditions	Reference
	Chloride Fractionation, 0° C.	
5.1	Precipitated from supersaturated solutions	(7)
5.3	Slow crystallization	(13)
4.5	Rapid crystallization	(13)
Av. 5.0		
	20° C.	
3.4	Rapid crystallization from supersaturated solutions	(10)
3.7	Slow crystallization from supersaturated solutions	(10)
3.7	Slow evaporation from saturated solutions	(10)
3.7	Fractional precipitation with HCl	(10)
3.6	Fractional crystallization by slow cooling 100° to 20°	(10)
3.4	Fractional crystallization by rapid cooling 100° to 20°	(10)
4.5	Slow evaporation from saturated solutions	(16)
Av. 3.7		
	90° C.	
2.3	Evaporation from saturated solutions	(10)
	Bromide Fractionation, 0° C.	
9.8	Slow crystallization	(13)
	20° C.	
6.8	Slow evaporation from supersaturated solutions	(10)
7.6	Slow evaporation from agitated saturated solutions	(10)
6.2	Slow evaporation from saturated solutions	(16)
Av. 6.9		
	85° C.	
4.4	Slow evaporation	(16)
3.1	Fast evaporation	(16)
5.7	Evaporation on water bath	(21)
Av. 4.4		
	Nitrate Fractionation, 0° C.	
1.8	Slow crystallization	(13)
2.0	Rapid crystallization	(13)
2.1	Rapid crystallization and long digestion	(13)
Av. 2.0		
	20° C.	
1.7	Rapid crystallization from supersaturated solutions	(10)
1.5	Slow crystallization from supersaturated solutions	(10)
1.4	Slow evaporation from saturated solutions	(10)
1.3	Slow evaporation	(13)
1.5	Rapid evaporation	(13)
Av. 1.5		

precipitated with their corresponding distribution coefficients and extrapolating to 0% salt precipitated. The limiting values are given in Table IV. At a particular temperature and for a particular salt the limiting distribution coefficients are not identical because of the variety of fractionation conditions used. The average values shown in Table IV are probably not too accurate; however, for each salt it is obvious that the limiting distribution coefficient is dependent upon the temperature at which the fractionation was made.

The effect of temperature on the concentration of radium by the fractional precipitation of several barium-radium salts (chromates, chlorides, bromides, and nitrates) is shown in Figure 3. An increase in limiting distribution coefficient with decreasing temperature is observed, indicating an increasing solubility differential between radium and barium salts with decreasing temperature. In addition, it can be seen from Figure 3 that fractionation of the chromates or bromides is about equally efficient either of which is better than the fractionation of the chlorides or nitrates.

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Methods for Determining Hydrocarbons and Phenols in Water

Report of the Subcommittee on Refinery Effluent–Water Analytical Methods, Committee on Analytical Research, Division of Refining, American Petroleum Institute

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THE necessity for controlled disposition of waste waters is recognized by industry. It is essential for good public relations, and for preserving rivers and lakes in such a condition that they may continue to serve the needs of society. The petroleum industry has a record of achievement in the field of waste disposal. Early developments in oil-water separators have been improved and other waste-treatment methods have been devised in recent years. Regulatory bodies in a number of states have set purity standards for waste effluents. Obviously, test methods are necessary for measuring the performance obtained in waste-treatment processes and for determining the extent to which these standards are met. The composition of waste effluents is complex and the low concentrations of components make it difficult to obtain analytical accuracy.

Recent advances in stream-pollution abatement have brought the industry to a point where future progress will be dependent upon the development of new analytical techniques having greater sensitivity and accuracy for hydrocarbons and phenols (the chief refinery offenders). For instance, for control of refinery waste oil determinations accurate to a few parts per million are desirable, and when drinking water supplies are being tested it is desirable to have methods that will measure a few parts per billion of either hydrocarbons or phenols.

Because this problem is common to most petroleum refineries, a number of laboratories, working cooperatively through the American Petroleum Institute's Committee on Analytical Research, have been investigating the analytical aspects of this problem since early in 1948. The material presented here is the result of this cooperative program, out of which have come analytical methods which more nearly approach the accuracy required for today's waste-control programs. The work of the subcommittee has consisted of stimulating and initiating analytical research in the participating laboratories and of cooperatively evaluating the techniques made available. Although the work of the group is continuing, a report should be valuable at this time, as the subcommittee has been responsible for the development of five new analytical methods and has cooperatively tested two other procedures, which were then combined into a sixth method.

In order to assist petroleum refiners in their efforts to remove oil and phenols from refinery effluent waters, a group of laboratories working cooperatively through the American Petroleum Institute's Committee on Analytical Research has developed or evaluated six new methods for determining oil or phenols in water. Some of these are rapid methods which give good accuracy on oils in concentrations above 1 p.p.m. Others employ expensive apparatus but are capable of determining a few parts per billion of either oil or phenols. These analytical techniques should be of material aid in today's pollution-abatement programs, although to date they have been tested chiefly on synthetic mixtures containing pure water rather than on refinery effluent waters.

Specifically, the work of the group has consisted of:

1. Initiation of research resulting in the development of an infrared method for hydrocarbons in concentrations as low as 0.1 p.p.m. and an infrared method for phenols in concentrations as low as a few parts per billion. These methods have been published, but the results of some cooperative work on hydrocarbon determination are given.
2. Cooperative testing of a modification of a published extraction-evaporation method for determination of oil in water in concentrations above 5 p.p.m. This method was found to be satisfactory for the ordinary refinery effluent waters, where large amounts of volatile contaminants are not present.
3. Initiation of research resulting in a method for determination of oil in water involving extraction and measurement of density. This method was cooperatively tested and found to be very good for all types of samples.
4. Initiation of research resulting in a mass spectrometer method for determining a few parts per billion of volatile contaminants in water.
5. Initiation of research resulting in an ultraviolet method for determining a few parts per billion of phenols in water.

HYDROCARBONS IN WATER

At the outset of this work methods for determining hydrocarbons consisted chiefly of gravimetric or volumetric techniques employing extraction or distillation (*1*), and were limited to oil concentrations above 1, and usually above 10, parts per million. In most cases, volatile components in the oil were lost during the procedure. In 1949 Kirshman and Pomeroy published an extraction method (*6*) which was sensitive to 1 p.p.m., but their definition of the "oil" and the absence of any provision for recovery of volatile oils placed a definite limitation on the application of the method.

Infrared Method. As a part of the activities initiated by this subcommittee, work was started on the development of an infrared method for determining both oil and phenol. The results of this work were published by Simard, Hasegawa, Bandaruk, and Headington in 1951 (*15*, *16*). This method was shown to be reliable for oil concentrations as low as 0.1 p.p.m. and to have an inherent error of less than ±20% on a group of waste oils from a single petroleum refinery. The chief source of error appeared to be the variation in the absorptivity of different oil samples at 3.4 microns. In order to check this, the absorptivity was measured on 22 oil samples submitted by members of the subcommittee, taken from the oil separators in the waste-disposal systems of the refineries of five different companies employing widely different processing methods. The variation in the absorptivities of these oil samples is shown in Table I, where the maximum deviation from the mean is seen to be 20%, and the standard deviation 10%. It is therefore concluded that the deviations between oils taken from various sources in a single refinery are approximately those that could be expected from one petroleum refinery to another and that the accuracy of the method is at least as good as that of the other methods presented.

Although very useful for reference purposes and where high sensitivity is needed, a procedure involving the use of an infrared spectrophotometer is not a satisfactory answer to the problem of analytical methods for waste control. Many laboratories have neither the funds available for the purchase of such equipment nor the personnel trained to operate and maintain it. It was therefore deemed advisable to seek additional methods which could be carried out by a technician in any chemical laboratory.

Benzene Extraction Method. A rather extensive evaluation program was carried out on a method which was submitted to the group and subsequently published in 1951 by Musante (*12*). This procedure involved direct extraction of a water sample with benzene, followed by evaporation of the benzene in equipment designed to minimize the loss of the more volatile fractions of the oil.

Three standard samples were used to test this and subsequent methods. The first sample was an SAE 70 heavy motor oil containing no measurable volatile fraction which would be lost during the benzene removal. The second sample consisted of 2 parts of the same heavy motor oil mixed with 1 part of kerosene. The third sample was composed of 1 part of the heavy motor oil, 1 part of kerosene, and 1 part of motor gasoline. These three oils were to be mixed with water in concentrations of from 10 to over 100 p.p.m. and analyzed by five laboratories. The three oil samples were sent to the five different laboratories together with detailed instructions. These instructions included directions for making the blends by weighing the oil into a vessel of the proper size containing cold distilled water, followed by vigorous

Table I. Oils Separated from Refinery Effluent Waters

Sample Source	Refinery Operations Involved	Absorptivity, 10 P.P.M. in CCl_4	Deviation from Mean %
Laboratory 4			
Sample 1	Catalytic and thermal gasoline	0.071	−10
Sample 2	Crude topping and lube oil distillation	0.073	−8
Sample 3	Duosol refining	0.086	+9
Sample 4	Acid treating area	0.080	+1
Sample 5	Catalytic cracking and H.F. alkylation	0.063	−20
Laboratory 5			
Sample 1	Slop oil from main separator	0.069	−13
Sample 2	Slop oil from API separator	0.078	−1
Laboratory 6			
Sample 1	.....	0.072	−9
Sample 2	.....	0.070	−11
Laboratory 1			
Sample 1	Lube oil and cracked gasoline treating	0.077	−2
Sample 2	Straight-run distillation operations	0.088	+11
Sample 3	Thermal and catalytic cracking operations	0.074	−6
Sample 4	Final separator box	0.080	+1
Laboratory 7			
Sample 1	No. 6 separator	0.076	−3
Sample 2	No. 7 separator	0.075	−4
Sample 3	Methyl ethyl ketone sewer	0.094	+15
Sample 4	Soap and acid plant sewer	0.074	−5
Sample 5	Pipe still skim	0.091	+12
Sample 6	No. 1 sewer	0.092	+13
Sample 7	Acid plant sewer	0.071	−8
Sample 8	Ballast wharf	0.082	+3
Sample 9	Paraffin sewer	0.093	+14
	Mean value	0.079	
	Max. deviation from mean		20
	Standard deviation		10

Table II. Benzene Extraction Method

Cooperating Laboratory	Oil 1[a] Oil added, p.p.m.	Oil found, p.p.m.	Found, %	Oil 2[b] Oil added, p.p.m.	Oil found, p.p.m.	Found, %	Oil 3[c] Oil added, p.p.m.	Oil found, p.p.m.	Found %
1	9.9	15.3	155	51	67	131	100	87	87
	10.0	15.6	156	48	55	115	108	100	93
2	13.1	24.8	189	63	67	106	96	80	83
	7.7	24.8	322	58	63	109	98	74	76
							106	80	75
3	8	8.9	111	13	11.3	87	12	6.0	50
	12	12.4	103	47	48	102	15	9.0	60
	16	16.2	101	54	48	89	59	33	56
	98	96	98	94	94	100	62	43	69
	102	111	109	115	125	109	100	80	80
				133	145	109	107	79	74
4	9.2	8.5	92	38	41	108	68	60	88
	8.5	9.5	112	47	49	104	72	62	86
	11.5	13.2	115	52	55	106	114	95	83
	13.2	18.0	136	52	58	112	133	106	80
	12.8	9.8	77	54	52	96			
	15.8	14.7	93	54	57	106			
				81	80	99			
				54	59	109			
5	10.7	10.6	99	45	40	89	106	73	69
	10.9	10.6	97	59	48	81	100	66	66
Mean value			127			103			75
Max. deviation from mean			195			28			25
Standard deviation			56			11			12

[a] Heavy motor oil.
[b] 2/3 heavy motor oil, 1/3 kerosene.
[c] 1/3 heavy motor oil, 1/3 kerosene, 1/3 motor gasoline.

mechanical agitation to disperse the oil in the water as completely as possible. The extraction was to be carried out in the vessel in which the blend was made, in order to prevent losses of oil which would be inevitable if the sample were transferred from one container to another. The oil was to be added by means of a 1-ml. hypodermic syringe.

The results of these tests are shown in Table II; recoveries of the known amounts were high in the case of nonvolatile oil, good in the case of the oil containing kerosene, and low in the oil containing gasoline. The high results on the heavy motor oil sample were due chiefly to a few very high results obtained by laboratories 1 and 2 on samples of low oil content. These are not considered representative of the accuracy that can be obtained on this type of sample, because both laboratories used only half the size of sample specified in the written procedure. The data obtained by laboratories 3, 4, and 5 are believed to be much more representative in this respect. Although not shown in the table, the mean recovery for these three laboratories on sample 1 was 103% and the maximum deviation was 33%.

Results on sample 3 were consistently low, indicating a high loss of the gasoline fraction. This was to be expected, as the method was not intended for hydrocarbons of high volatility. Because the more volatile fractions may soon be lost from the water by evaporation, there might be some question as to whether recovery of volatile oil is necessary for such a control method. For applications where refinery losses are being measured, however, volatile oil recovery in an analytical method is highly desirable.

Reflux Distillation–Extraction Method. The benzene extraction method of Musante was modified by preceding it with a reflux distillation through a modified ASTM dilution trap, in accordance with a procedure submitted to the group by Neusbaum (*13*). The combined method was then tested cooperatively and the results are shown in Table III. The method was subsequently adopted by the Committee on Disposal of Refinery Wastes of the American Petroleum Institute as one of two approved methods and will be made available through that organization (*2*). Table III shows some improvement in the recovery of the volatile fraction when the refluxing step is added to the benzene extraction procedure. The refluxing step also serves to distinguish between volatile and nonvolatile oil, although the distinction between the two is somewhat arbitrary. It is believed that the accuracy shown in Table III would be satisfactory for the ordinary samples that would be encountered in a petroleum refinery.

Extraction-Pycnometer Method. In the search for a simple method which would give the least possible error on sample containing volatile hydrocarbons, a method was developed in one laboratory which involves direct extraction with carbon tetrachloride. The weight of an accurately measured volume of the carbon tetrachloride extract is then compared to that of an equal volume of the pure solvent and the assumption of an average specific gravity of the oil enables one to calculate directly the amount of oil in the water (*7*).

Cooperative work on this method has shown it to be very promising and particularly well adapted to handling waters contaminated with

Table III. Reflux–Benzene Extraction Method

Cooperating Laboratory	Total Oil, P.P.M. Added[a]	Found	Oil Found, % Volatile	Nonvolatile	Tota
2	105	105	..	..	100
	99	96	..	..	97
4	16	13	..	..	81
	21	18	..	..	86
	28	22	..	..	79
	44	37	..	..	84
	68	56	..	..	82
	77	65	..	..	84
	83	70	..	..	84
	101	90	..	..	89
	112	96	..	..	86
	108	80	..	..	74
	112	92	..	..	82
	123	95	..	..	77
	124	100	..	..	81
	132	112	..	..	85
	132	128	..	..	97
	133	121	..	..	91
	149	125	..	..	84
	157	140	..	..	89
5	120	102	41	44	85
	120	100	43	40	83
	120	107	46	43	89
	120	102	43	42	85
6	11.8	8.2	17	53	70
	11.8	6.7	13	57	57
	46.5	31.3	29	36	67
	51.0	33.7	23	43	66
	71	48	30	38	68
	74	50	29	38	67
	99	68	30	39	69
	105	74	32	38	70
	149	107	36	36	72
	160	113	37	34	71
Mean value					80
Max. deviation from mean					23
Standard deviation					10

[a] 1/3 SAE 70 motor oil, 1/3 kerosene, and 1/3 gasoline in all cases.

Table IV. Extraction-Pycnometer Method

Cooperating Laboratory	Oil 1[a] Oil added, p.p.m.	Oil found, p.p.m.	Found, %	Oil 2[b] Oil added, p.p.m.	Oil found, p.p.m.	Found, %	Oil 3[c] Oil added, p.p.m.	Oil found, p.p.m.	Found, %
1	10	10.1	101	10	11.6	116	10	11.5	115
	100	110.6	111	100	111.6	112	100	102.3	102
8	20	18	90	20	20	100	20	19	95
	84	82	98	20	21	105	21	21	100
	122	122	100	63	64	102	85	90	106
				102	102	100	85	90	106
							91	90	99
							99	93	94
9	51.6	51.9	101	66.8	58.9	88	36.4	36.5	100
	101.6	101.3	100	87.3	90.5	104	54.8	51.0	93
				118.5	115.8	98	62.3	62.2	100
				152.3	134.1	88	89.8	89.4	100
							95.2	102.7	108
							100.2	100.7	100
10	10.5	10.9	104	10.8	10.3	95	11.0	13.8	125
	121.0	145.8	120	115.0	105.3	92	97.4	107.1	110
11	18.4	16.0	87						
	74.8	62.0	83				60.4	55.0	91
	84.2	81.6	97				136.2	131.0	96
7	10	16	160	10	12	120	10	12	120
	10	16	160	10	11	110	10	11	110
	10	10	100	75	67	89	75	64	85
	75	66	88	75	67	89	75	67	89
	75	64	85	150	142	95	150	132	88
	150	147	98	150	128	85	150	136	91
	150	146	97						
Mean value			104			99			101
Max. deviation from mean			56			21			24
Standard deviation			21			10			10

Mean value for all oils = 102
Standard deviation for all oils = 14

[a] Heavy motor oil.
[b] 2/3 heavy motor oil, 1/3 kerosene.
[c] 1/3 heavy motor oil, 1/3 kerosene, 1/3 gasoline.

volatile oils. The cooperative data obtained on this method by the subcommittee (Table IV) show that the recoveries on all the oil samples were good and that the recoveries on the sample containing one third gasoline were fully as good as those for the less volatile oils. Opinion differed among the different laboratories as to the skill required to use the method. Laboratory 11 remarked, "We consider the method extremely ingenious in its simplicity of manipulation and calculation." Laboratory 10, however, said, "Results with accuracy of the order reported were possible only after much experience and then only by men who we know have skill above that of the average analyst." On the whole, the comments indicated that more analytical skill is required to use this method than the reflux distillation–extraction method. It is probable, however, that in many cases this requirement of additional skill will be more than compensated by the improved accuracy on volatile contaminants.

Mass Spectrometer Method for Trace Amounts of Volatiles. The above methods provide a variety of techniques for determining oil in water in amounts down to 100 parts per billion. In some cases, however, when claims are made that drinking water sources have been contaminated by such materials as gasoline, it may be desirable to have a method that will detect quantities smaller than 100 p.p.b. and give some indication of the nature of the contaminant. As a part of the work of this subcommittee a method was developed by one laboratory wherein volatile hydrocarbons are stripped from the water by a stream of hydrogen and examined in a mass spectrometer (*10*). The method is capable of measuring and distinguishing between such substances as gasoline, natural gas, dry cleaning fluids, and even furnace oil at concentrations as low as 10 parts per billion and is suitable for materials boiling below 200° C. This method has not yet been cooperatively tested.

PHENOLS IN WATER

Prior to the work of this group, the methods used for determining phenols in water consisted of the colorimetric Gibbs method (*4*) and the Scott modification thereof (*3*); the method published by Lykken, Treseder, and Zahn (*8*) employing a modification of the nitrosophenol method of Stoughton (*17*); and the aminoantipyrine method of Gottlieb and Marsh (*5, 9*). Murray (*11*) also describes a method for determining phenols in gasoline employing an ultraviolet absorption technique.

Two additional methods were developed as a direct result of this subcommittee's activities in the field of effluent water analysis. The first was the infrared method referred to above in conjunction with oil in water analysis (*15, 16*). This method employs bromination of the phenols, followed by their extraction with carbon tetrachloride and measurement of their infrared absorption at 2.84 microns. The second method (*14*) employs extraction of the alkaline sample with carbon tetrachloride to remove oil, followed by extraction of the phenols from the acidified sample with tributyl phosphate. The extract is then analyzed by the ultraviolet method of Murray (*11*), involving comparison of the ultraviolet absorption of two portions of the phenol extract, one at pH 12 and the other at pH 5, to measure the phenol concentration. Both methods are applicable to concentrations of a few parts per billion of phenols. These methods are so new that there has been no opportunity to evaluate and compare them by cooperative testing.

CONCLUSIONS

This work has resulted in methods substantially better than those previously available, although further testing on actual refinery effluent waters will be necessary before their applicability is fully established. The new methods for determining oil content approach what is currently required as regards accuracy and speed. The methods for phenols appear to be more accurate and reliable but require spectroscopic equipment which smaller laboratories may not have.

In spite of this, however, much work remains to be done in this field. For instance, waste waters from petroleum refining operations may contain small amounts of nitrogen and sulfur compounds. Oxygenated compounds, other than phenols, can also be present. Analytical methods are needed for as many of these compounds, or compound types, as is possible, and methods are desired which will yield qualitative as well as quantitative information. The mass spectrometer method is a first step in this direction but is, unfortunately, limited to volatile materials. As an example of the need for qualitative information, refinery effluents are sometimes discharged into streams which have previously been polluted by trace amounts of industrial wastes or even sewage. For the protection of the refiner it would be very helpful to be able to distinguish between vegetable or sewage fats already in the water and the hydrocarbons and their derivatives which might be attributed to the petroleum refiner. These are difficult problems, but should not be looked upon as unsolvable with today's modern analytical tools and techniques.

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Precision Recording Refractometer for Chromatographic Analysis

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An instrument has been developed, which is capable of continuously and accurately plotting refractive index changes relative to any reference state in any nonopaque liquid stream, against mass of the liquid. Linearity and zero stability in each coordinate are adequate; maximum sensitivity is $(3.54 \pm 0.04) \times 10^{-6}$ refractive index unit per division (0.05 inch) for the refractive index coordinate and 56 ± 5 mg. per division (0.05 inch) for the mass coordinate. With most organic substances in acetone solution the refractive index sensitivity corresponds to a change in concentration of approximately 0.020 mg. per ml. of acetone per scale division. This apparatus is particularly useful in chromatographic investigations and analyses.

THE chromatography of colorless compounds has long been burdened with tedious techniques of fraction collection and estimation. In an attempt to alleviate some of this drudgery and the attendant loss of valuable man-hours, as well as to improve both the precision and reliability of the results, the instrument here described was designed and constructed.

In following the progress of a chromatographic process (frontal analysis, elution analysis, or displacement development) the solute concentration or nonsolvent mass per unit mass (or volume) of solvent is the quantity most often required. This is the "liquid chromatography" of Tiselius (*8*). Other properties directly related to solute concentration, however, are more readily amenable to continuous determination. Among these are radiation absorption (ultraviolet, visible, and infrared) or better, the more general refractive index measurement.

Instruments (mainly manual, a few recording) using refractive index as the concentration-determining property, have been described by Tiselius and Claesson (*9*), Dutton (*2*), Claesson (*1*), Zaukelies and Frost (*10*), Jones, Ashman, and Stahly (*5*), Thomas, O'Konski, and Hurd (*7*), Holman and Hagdahl (*4*), and others. In designing and constructing their recording differential refractometer, the authors have endeavored to avoid weaknesses and shortcomings inherent in previous instruments, without making the apparatus unduly cumbersome and complicated.

In order to obtain an instrument of high mechanical and electrical stability, with attendant high sensitivity and precision, they felt that the following features, based upon sound, essential principles, should be incorporated into its design. In the case of the refractive index coordinate, a single source of monochromatic radiation and a single receiver should be used. Gradients in the sensitivity of the photoreceptor surface (cathode) should be avoided by the use of an integrating sphere. The instrument should be of the null type, correction and measurement being made only when there is an appropriately modulated alternating current error signal. General noise should be minimized by careful thermostating of the refractometer cell, reduction of schlieren in the light path, and use of narrow band amplifiers. The differential refractometer cell should be one fused unit of borosilicate glass, designed to be as small as practical—i.e., small holdup.

In the case of the flow coordinate, a device which measures directly the mass or volume of the effluent is to be preferred to the use of time as the horizontal coordinate, because in general it is very difficult and sometimes even impossible to maintain a rigorously constant flow rate through certain types of chromatographic columns. Methods based on drop counting suffer from changes in drop size due to evaporation (with volatile solvents) and/or surface tension variations of the effluent. A strain gage, which can be connected so that the output voltage is pro-

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portional to mass, is, therefore, used in the recording refractometer as the mass-sensing element.

DESCRIPTION OF INSTRUMENT

By reference to the block diagram of Figure 1, the over-all functioning of the recording differential refractometer may be visualized.

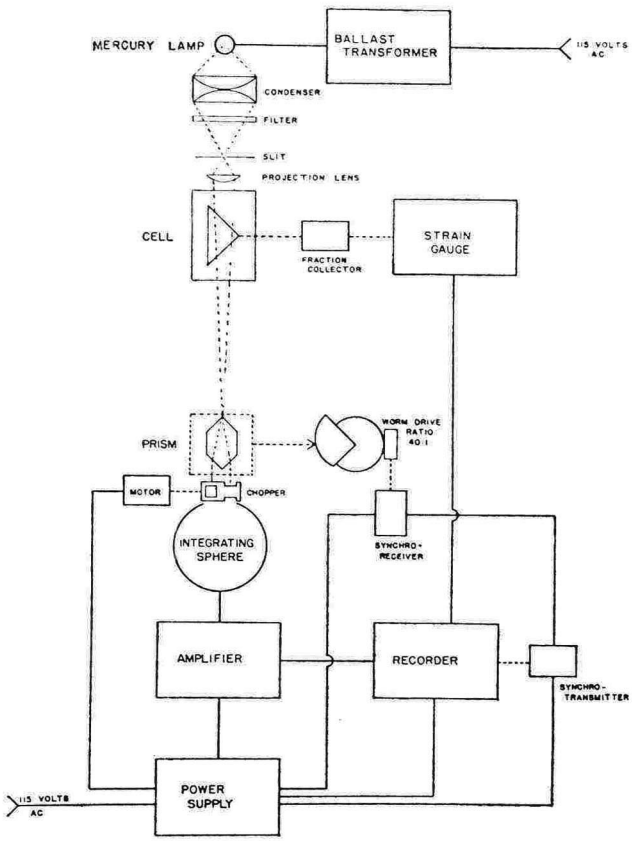


Figure 1. Block Diagram of Complete Recording Refractometer

At the top of the diagram, light from the source, a General Electric H-4 mercury lamp powered by its ballast transformer, is focused on the slit in the usual manner with a condensing lens. A narrow-band interference-type filter (Baird Associates, Inc., 33 University Road, Cambridge 38, Mass.), placed between the condensing lens and the slit, isolates the 5461 A. line of the mercury source.

Light from the slit enters the differential refractometer cell (made to design by Phoenix Precision Instrument Co., 3803 North Fifth St., Philadelphia 40, Pa.), shown in Figure 2, where it suffers deflection corresponding to the difference between the refractive index of the external comparison solvent and the solution passing through the internal hollow prism. The cell is of fused borosilicate glass, and is divided into two compartments, an inner, hollow, right 45° isosceles prism, and an outer, solvent compartment. The hollow prism is 8 mm. in height, and has a base of 10 mm., an altitude of 5 mm., and a total volume, including the side arms, of 0.50 ml. The entrance and exit joints for the prism are $ 7/25 ground-glass joints with mercury seals, and connecting tubing is 1-mm. capillary. The outer cylindrical cell compartment, used for the comparison solvent, has a volume of 18.2 ml. and is fitted with plane parallel entrance and exit windows and $ 7/25 ground-glass joints connected with 2-mm. capillary. The cell body has a diameter of 28 mm. and a length of 40 mm. The inner prism tubulatures rise 40 mm. above the top of the cell, while the outer tubulations are 80 mm. high. Both end windows and side windows of the prism, through which the light beam passes, are of good optical quality. A diaphragm, consisting of a sheet of aluminum foil attached to the cell window farthest from the light source and having a round hole 4.0 mm. in diameter, limits the cell aperture to 4.0 mm.

The cell is mounted in a machined brass block in which it is rigidly set in hard wax. This brass block is mounted rigidly in a steel frame which has its own suspension, attached to the optical bench, and is mechanically independent of the constant temperature bath in whch the cell and frame are immersed.

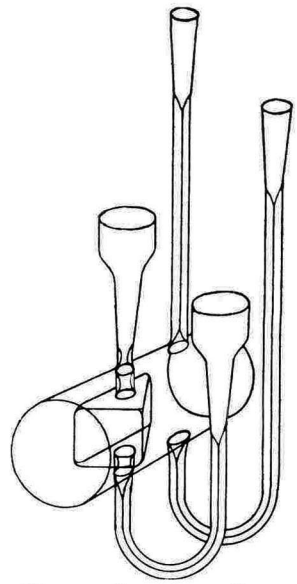


Figure 2. Borosilicate Glass Flowing Differential Refractometer Cell

In Figure 3 the cell is shown mounted in its supporting assembly, and a small chromatographic column is in place on top of it.

The constant-temperature bath itself stands upon a heavy reinforced supporting bench to which the optical bench is bolted, and maintains the temperature of the bath liquid well within 0.01° C. of the desired temperature, usually a few degrees above average room temperature. Plane glass side windows in the constant-temperature bath are mounted upon threaded telescoping tubes, so that they may be adjusted close to, but yet not touching, the end windows of the differential refractometer cell. This arrangement minimizes schlieren introduced into the light path by temperature gradients in the stirred bath water, yet avoids the transmission of vibration from the constant temperature bath walls to the cell. The use of two tanks, one inside the other (the outer being stirred, the inner not) was found very unsatisfactory because of considerable noise due to the slow circulation of convection currents in the inner tank.

The effluent from the chromatographic column is conducted first through a 5-foot coil of stainless steel hypodermic tubing, 20-gage, immersed in the constant-temperature bath, then into the bottom of the cell where it rises slowly into the hollow prism. (The 5-foot length of tubing was necessary because the instru-

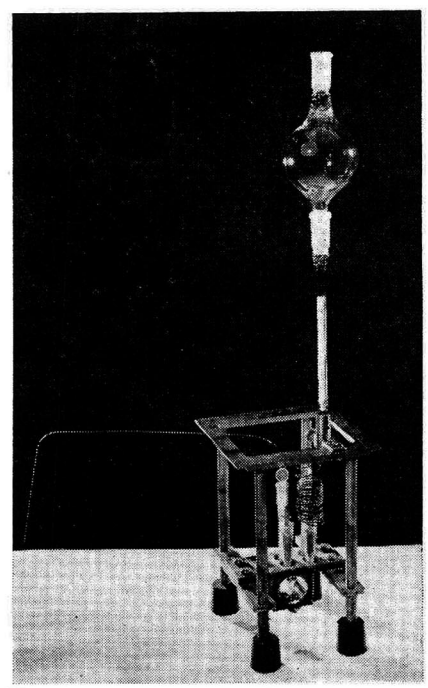


Figure 3. Recording Refractometer Cell Assembly

Small chromatographic column (5 grams of alumina packed 1 × 11 cm.) is mounted over cell

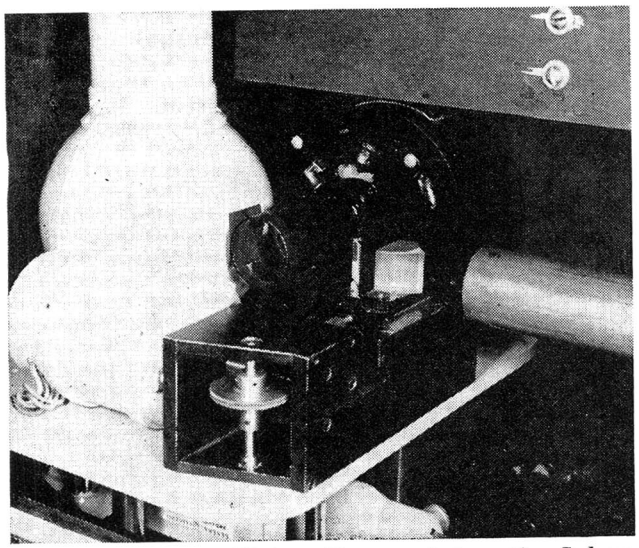


Figure 4. Hexagonal Prism-Chopper–Integrating Sphere Assembly

ment was designed for fast as well as slow rates of flow.) This arrangement brings the effluent to the bath temperature, effectively clears air bubbles from the cell as soon as they appear, and avoids density inversions in the fronts where density of the eluate gradually increases. A second short length of stainless steel hypodermic tubing conducts the eluate from the top of the prism into the fraction collector, which is suspended from the mass-sensing strain gage. Metal to glass connections are made through the use of stainless steel $ 7/25 joints made in the machine shop.

A small projection lens, located between the slit and the differential refractometer cell, focuses the slit image upon the apex of the hexagonal prism (*8*), which is the deflection-detecting or error-reducing element in the system. This hexagonal prism is mounted upon a platform which slides in precision-ground ways in the same plane as that in which the light beam deflection occurs. The slit image, 2.5 cm. long and a few tenths of a millimeter wide when focused precisely upon the apex of the prism, is split into two parallel beams of equal intensity, which emerge from opposite sides of the prism (because of crossover within the prism) about 23.5 mm. apart. Each beam is alternately chopped twice in each revolution by a 60-cycle cylinder-type chopper driven at 1800 r.p.m. and then enters the integrating sphere where the radiation is detected by the RCA 5819 photomultiplier tube. A photograph of the hexagonal prism-chopper–integrating sphere assembly is shown in Figure 4.

With the slit image precisely centered upon the apex of the hexagonal prism, both emergent beams are of equal intensity and the light seen by the photomultiplier tube in the integrating sphere has no 60-cycle component. Any intensity unbalance in the two beams, however, caused by displacement of the slit image to one side or the other of the apex of the hexagonal prism, results in introduction of an alternating component of 60 cycles into the light entering the integrating sphere. This 60-cycle component is amplified by the photomultiplier and its following, high-gain, tuned (60-cycle) amplifier (see Figure 7) and energizes the control winding of the two-phase pen-drive motor in the strip-chart recorder.

Both the synchronous chopper motor and the pen-drive motor of the strip-chart recorder are synchronized with the 60-cycle line frequency, and the 60-cycle, cylinder-type chopper is phased so that the 60-cycle signal, when one is produced by unbalance in the two beams emerging from the rear of the hexagonal prism, always lags or leads the current in the line-powered exciting winding of the two-phase pen-drive motor by 90°. Thus the direction of pen travel in the recorder is phase-sensitive and is determined by the direction of the movement of the slit image. Proper phasing between the chopper motor and the pen-drive motor is obtained at starting by the operation, when necessary, of the phasing switch shown in the schematic diagram of Figure 7. This reverses the phase in the line-energized winding of the pen-drive motor of the Brown recorder.

A Selsyn transmitter-receiver combination links the pen position electromechanically to the position of the hexagonal prism, as shown by the block diagram of Figure 1. The hexagonal prism table itself is spring-loaded against an Archimedian spiral cam (radius increases 0.0020 inch for each degree of rotation for this particular cam) which is driven by the Selsyn receiver through a 40 to 1 reducing worm drive. The mechanical linkage is such that full scale pen travel corresponds to 1240° of rotation of the Selsyns, 31.0 degrees rotation of the cam, and 0.0620 inch or 1.57-mm. displacement of the hexagonal prism. This corresponds to an angular deviation of the light beam at the cell of only 0.00154 radian or 0.0883 degree for an optical lever length of 1 meter (cell to prism). One division on the recorder chart (220 divisions full scale) thus corresponds to a displacement at the detector of 7.14 microns or a deviation of 1.44 seconds of arc.

By application of the approximate relationship: angle of deviation (radians) = 2 tan a $(Ns\text{-}No)$ (*6*), where a is the angle of incidence at the hollow prism (45°), we get for $(Ns\text{-}No)$ or Δn 0.000770 refractive index units change for full scale or 3.50×10^{-6} refractive index unit change per chart division at maximum sensitivity (using chart paper having 220 divisions for eleven inches). This value agrees well with the experimentally found value of $(3.54 \pm 0.04) \times 10^{-6}$ using sodium chloride solutions of known refractive index in the range of concentrations from 0.01 to 0.07M.

The primary sensing element in the mass collection system is a

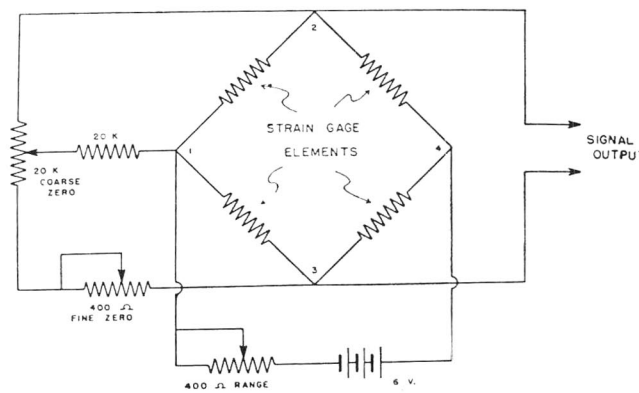


Figure 5. Schematic Diagram of Strain-Gage Circuit

Output goes directly to standard 5-mv. input of strip-chart recorder and controls chart position.

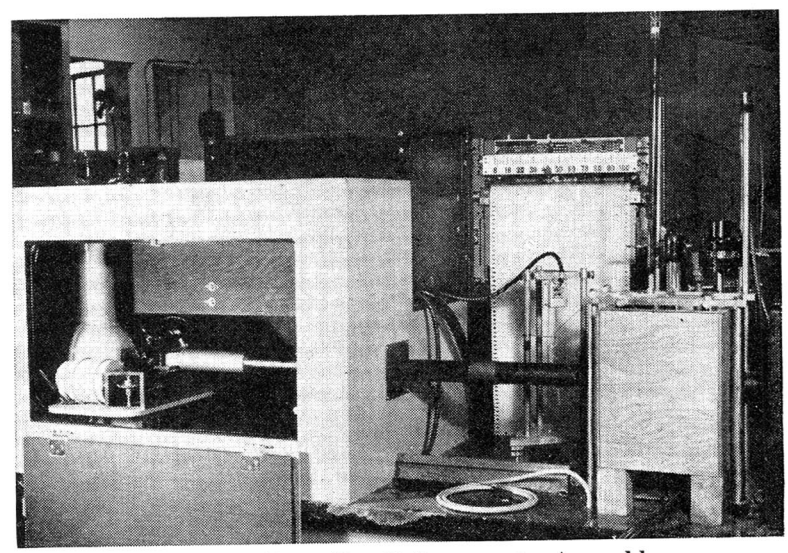


Figure 6. Recording Refractometer Assembly

Large chromatographic column is shown mounted in place over recording refractometer cell.

so-called "unbonded strain gage," shown in the schematic diagram of Figure 5.

The gage used by the authors is a Statham Model Gl-4–225 (Statham Laboratories, Inc., 9328 Santa Monica Blvd., Beverly Hills, Calif.) with a maximum load rating of 4 ounces (120 grams) and a resistance of approximately 225 ohms at input or output terminals. Other gages are available with maximum ranges of from 1.5 to 48 ounces. Thus with a collector of 40 grams, for example, a liquid mass of 80 grams may be collected using the 4-ounce gage.

As shown in Figure 5, the strain gage is powered by a 6-volt battery (large-capacity storage type for stability) and is provided with fine and coarse zero controls and a range control. The range control makes possible an approximately 1 to 3 variation in the output of the gage from approximately 50 to 150 μv. per gram in this particular circuit. The output of the gage goes directly to the standard 5-mv. direct current input terminals of the modified Brown strip-chart recorder, and controls thereby the chart position (mass or x coordinate) as explained more fully below. Consequently, the maximum and minimum range adjustments will provide for total loads of approximately 100 grams at 50 μv. per gram and 33 grams at 150 μv. per gram. Total chart travel is 30 inches or 77 cm. for 5.0-mv. input to the recorder, so that chart travel at the *maximum range* (minimum sensitivity) is approximately 0.30 inch or 7.7 mm. per gram, while at the minimum range (maximum sensitivity) setting it is 0.90 inch or 23 mm. per gram. Thus for liquids having a density of about unity the volume sensitivity of this apparatus is about 0.055 ml. per division.

The strip-chart recorder used was modified from a Brown, standard speed, 5-mv. strip chart model (Brown Instrument Division, Minneapolis-Honeywell Regulator Co., Philadelphia, Pa.) with automatic standardization. The pen-drive slide-wire has been removed and the pen-drive motor is driven directly by the 60-cycle tuned amplifier of the refractive index measuring system, as shown in Figure 7. A Selsyn transmitter, mechanically (nonslip cable drive) linked to the pen position, is mounted in place of the pen-drive slide-wire and controls the hexagonal prism position by electrical linkage to the Selsyn receiver, as shown in the block diagram of Figure 1. The Selsyns are standard Autosyn generator Type A (Marine Division, Bendix Aviation Corp., Brooklyn, N.Y.) units powered by the 60-cycle line supply.

The original synchronous chart drive of the Brown recorder was completely removed and replaced by a phase-sensitive drive

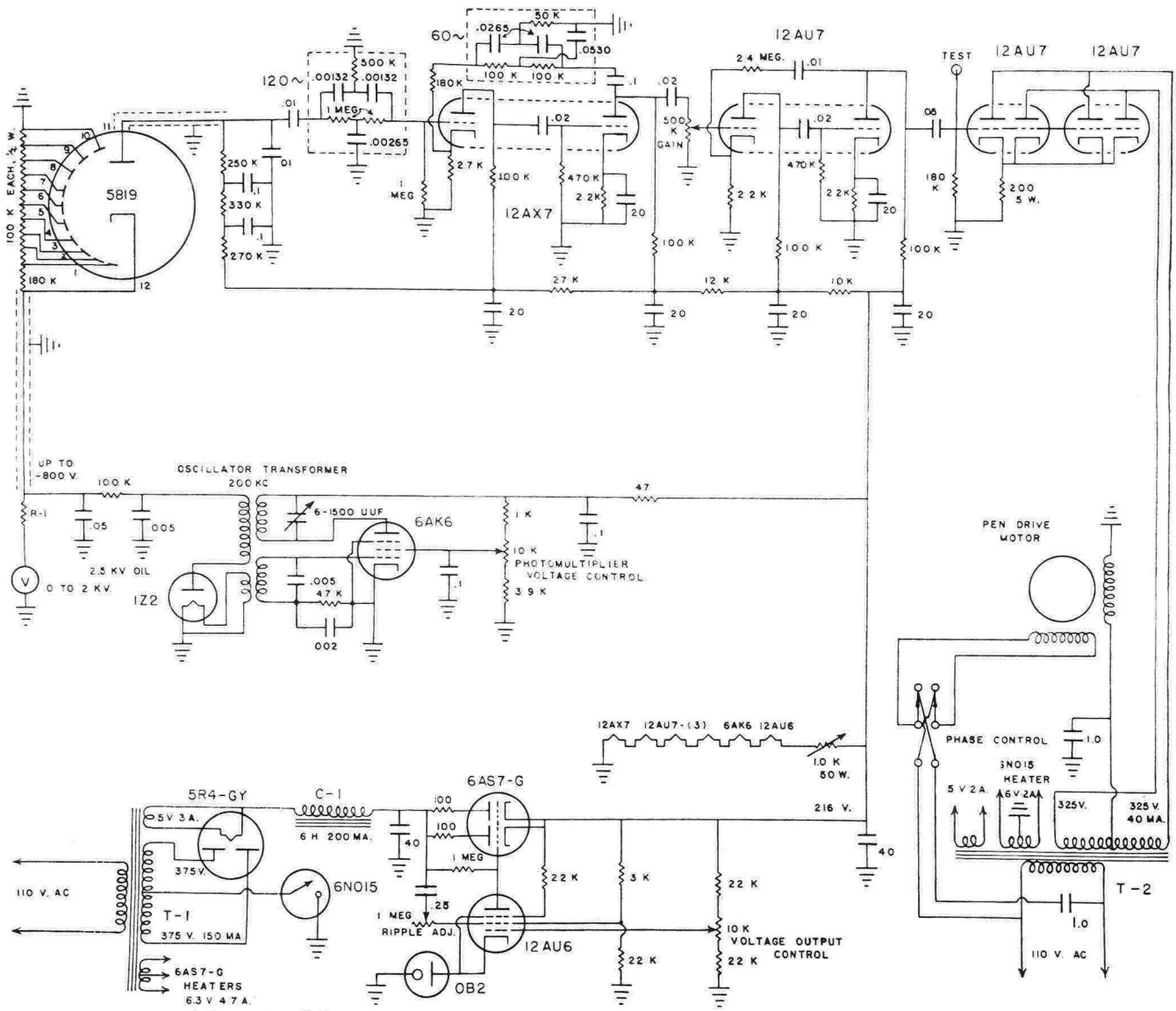


Figure 7. Schematic Diagram of Refractive Index Amplifier and Power Supplies

C-1. Thordarson choke T-20C55.
R-1. If necessary, is adjusted so that voltmeter *V*-1 will read photomultiplier voltage directly.
T-1. Thordarson transformer TS24R06.
T-2. Thordarson transformer TS24R01.
1Z2 tube. High-frequency, high-voltage rectifier manufactured by Chatham Electronics, Newark, N. J.
Resistors. 1-watt carbon. Value in ohms unless otherwise indicated, except that input resistors of amplifier are a low-noise type, Nobeloy. 50K and 500K resistors of filter should be padded for minimum response.
All capacitors valued in microfarads unless otherwise stated. Paper-oil except for 20- and 40-μfd. units, which are electrolytic.

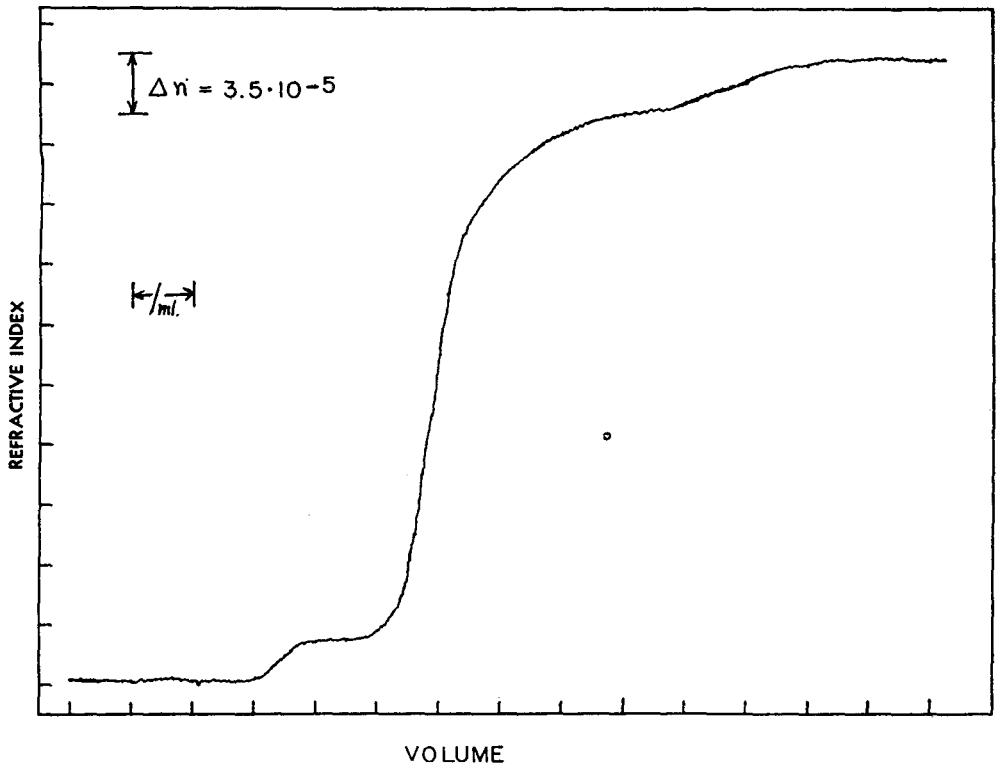


Figure 8. Frontal Analysis Recording Obtained with Recording Refractometer

Vertical coordinate represents refractive index (3.5×10^{-6} refractive index unit per division). Horizontal coordinate represents mass or volume (1.00 ml. of acetone per division). Curve is frontal analysis of impure sample of Kendall's compound A (11-dehydrocorticosterone) on specially treated alumina. Solution containing 2.0 mg. of compound A per ml. was used. Rate of flow, about 5 ml. per hour

system controlled by the output of the strain gage. A new two-phase drive motor, the remounted slide-wire from the pen-drive system, and the chart drum are all coupled together by a cable drive, so that 5 revolutions of the chart (30 inches) cover the full length of the slide-wire in 60 seconds. A clutch is provided in the chart drive for convenience in changing the chart setting. The chart-drive motor is now controlled by the amplifier originally used for the pen-drive motor, but modified to obtain increased gain by the substitution of a fourth stage of amplification for the original rectifier stage. Plate power for the amplifier is provided by the master regulated power supply shown at the bottom of Figure 7.

The original automatic standardization used in the pen-drive system has been transferred to the chart-drive system. The balancing rheostat is still driven by the pen-drive motor (a special relay switches it to the output of the chart-drive amplifier for this purpose), but the balancing rheostat clutch and the relay-releasing microswitch are now operated by an added 24-volt motor (powered by an added 24-volt transformer). A 20-minute timer normally controls the standardization cycle, but a manual standardizing switch is provided and the automatic standardization may be eliminated if desired by a switch which opens the timer power circuit.

The entire optical system and the refractometer cell are mounted upon a rigid, steel, optical bench 53 × 45 mm. in cross section and 192 cm. long. The cell itself is mounted 23 cm. beyond the slit, while the distance from the cell to the hexagonal receiving prism may be varied from 54 to 102 cm. to allow an almost twofold change in sensitivity. The light path between the cell and the hexagonal beam position-detecting prism is enclosed in a light-tight tube of 4-cm. diameter and the entire hexagonal prism-chopper-integrating sphere assembly is enclosed in a light-tight box in order to minimize noise from stray light and especially from air convection currents.

A photograph of the entire apparatus is shown in Figure 6.

For optimum performance it is recommended that the entire apparatus be assembled upon a heavy brick or concrete pier or heavy steel (reinforced against flexure) base in an air-conditioned room. Any heat-generating element, such as the chopper motor, should be mounted outside of the light-beam compartment so as to reduce noise from air convection. An evacuated tube in the path of the light beam may be desirable when air-convection noise is to be reduced to a minimum.

The schematic diagram of the refractive index servo, with its amplifier and power supplies, is shown in Figure 7.

The dynodes of the 5819 photomultiplier tube are supplied with up to 800 volts by the power supply unit in the center of the diagram. Here the output of the 6AK6 oscillator is stepped up by the 200-kc. coil and rectified by the miniature 1Z2. The filtered output, negative with respect to ground, is under the full control of the photomultiplier voltage control, as shown in the diagram.

The 60-cycle signal from the photomultiplier tube is amplified by the four voltage amplifier stages of the 60-cycle tuned amplifier at the top of Figure 7, and the unwanted 120-cycle signal is rejected by the parallel T filter at the input. The output of voltage amplifier stages drives a typical push-pull-parallel output stage, the output of which controls the two-phase pen-drive motor of the strip-chart recorder.

At the bottom of the schematic diagram (Figure 7) is the master-regulated power supply, which furnishes plate power to the amplifier of the mass detecting system, as well as to the units shown in the schematic diagram. Regulation is to within 0.5% for line voltage changes of from 105 to 120 volts.

The authors have found it convenient to use uniformly graduated chart paper (obtainable from Brown Instrument Division, Minneapolis-Honeywell Regulator Co., Philadelphia, Pa., recorder chart paper 5839-N, made to order), having 20 lines to the inch along each axis, in the recorder. Thus, one division equals 0.05 inch. All sensitivity and linearity figures in this paper are therefore stated in terms of these chart divisions.

OPERATIONAL CHARACTERISTICS

The refractive index coordinate was calibrated by measuring the deflections produced by several solutions of sodium chloride ranging from 0.01 to 0.07 *M* and yielded a good linear function of slope of $(3.54 \pm 0.04) \times 10^{-6}$ refractive index unit per chart division. This is indicative of the excellent sensitivity and adequate linearity of the apparatus. The chart scale (at maximum sensitivity) was covered from 28 to 199 divisions. Sensitivity in the case of the mass coordinate amounts to 18.0 ± 0.2 divisions per gram for weights of 1 gram and greater at maximum sensitivity (0.90 inch per gram or 23 mm. per gram). Below 1 gram the sensitivity falls off to a value of 15 divisions per gram for 100 mg., but the linearity is well within the value stated by the strain gage manufacturer of 1% or less of full scale. A 50-mg. change in mass at full load is easily detectable at the maximum sensitivity.

Noise in the refractive index coordinate is within 0.5% of full scale (see recordings), while in the mass coordinate it is unobservable at maximum sensitivity. Zero stability is adequate in both coordinates, provided equilibrium conditions are maintained in

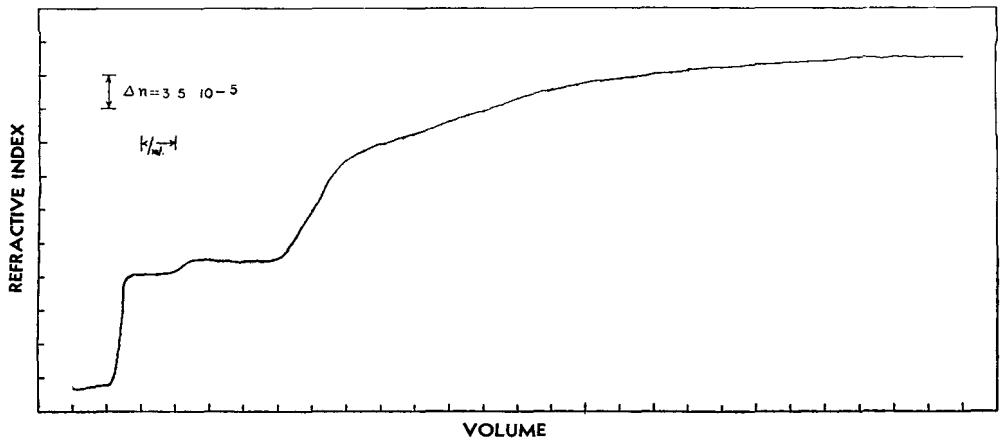


Figure 9. Frontal Analysis Curve of Mixture of Equal Parts of Progesterone Desoxycorticosterone, and Kendall's Compound S on 1.0 Gram of Alumina

Total concentration, 60 mg. in 30 ml. of acetone

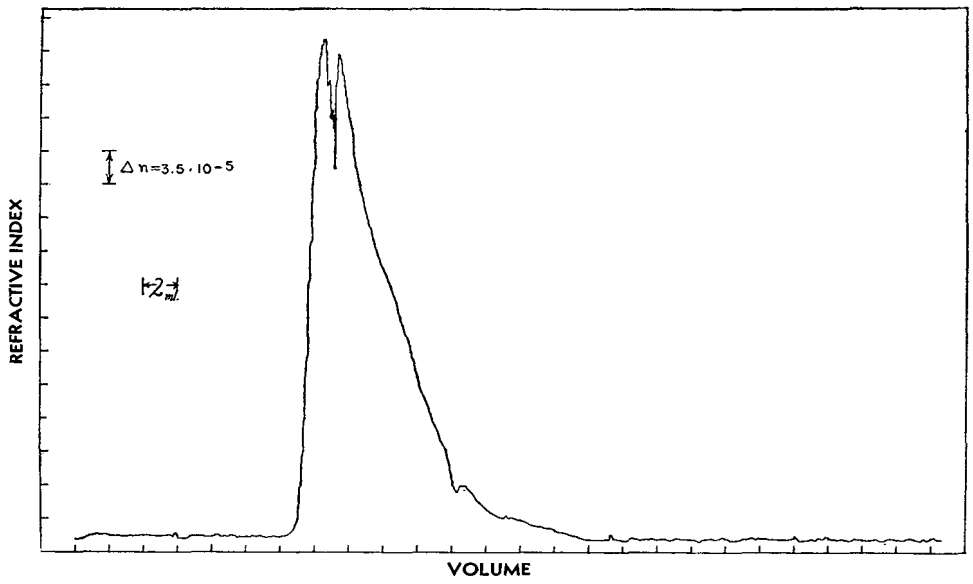


Figure 10. Elution Analysis Curve of Progesterone on Alumina

6.0 mg. of progesterone dissolved in 1.0 ml. of acetone was placed on top of a column of 20.0 grams of alumina, then eluted with acetone.

the refractive index system and the mass system is standardized occasionally. At maximum speed the pen covers its full range of 11 inches in 20 seconds, while the chart covers its maximum range of 30 inches in 60 seconds.

The authors have found it convenient to use with their recording refractometer borosilicate glass chromatographic columns constructed by them and ranging in capacity from a few tenths of a gram to over 100 grams (of alumina).

Each column has a capillary ⅋ 7/25 male joint sealed at the bottom, and a ⅋ 14/35 female joint sealed at the top. Bulbs of capacities ranging from 125 to 500 ml. and fitted with ⅋ 14/35 ground-glass joints at top and bottom are used as reservoirs for the solvents or solutions being passed through the columns. A small plug of glass wool at the bottom of each column retains the solid adsorbent. Every effort has been made to achieve the maximum elimination of dead spaces between the bottom of the column and the refractometer cell.

A typical frontal analysis curve obtained with the recording refractometer is shown in Figure 8. This curve was obtained by chromatographing a 0.20% solution of impure Kendall's compound A (11-dehydrocorticosterone) on 1.0 gram of acid-washed alumina at a rate of about 5 *ml. per* hour. The main wave is the front for compound A, while the small prewave and the small wave on top of the large wave represent impurities. A frontal analysis of a mixture of equal parts of progesterone, desoxycorticosterone, and Kendall's compound S on 1.0 gram alumina is shown in Figure 9. Total concentration was 60 mg. in 30.0 ml. of acetone. An elution analysis of progesterone on alumina is shown in Figure 10. Here 6.0 mg. of progesterone was dissolved in 1.0 ml. of acetone, placed on top of a column of 20.0 grams of alumina, and eluted with acetone. More detailed experimental work with this instrument will be forthcoming in future publications.

DISCUSSION

Although this instrument is highly satisfactory, experience has made it apparent that certain changes should be made to render it still more flexible and versatile. A greater mass range, perhaps from 30 to 300 grams full scale, as well as a more extensive refractive index range encompassing more concentrated solutions, would be useful. Important, too, would be redesign of the refractometer cell, so that concentration gradients within the flowing stream could be measured, giving curves which would be the first derivatives of those now obtained. This would be following the "crossing over" practice reported by Holman (*3*). This could be achieved by greatly reducing the volume of the hollow prism environment and interconnecting the two cell elements serially. The refractive index sensitivity might be conveniently changed by the use of a suitable lens system which would reduce the beam displacement by a known amount. It would be helpful if phasing between chopper motor and line frequency were automatic instead of manual.

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Mercury Pool Polarography

Ion-Amalgam Reductions Occurring at Surface of a Large Stationary Mercury Pool

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In order to extend the range of polarographic methods, possible analytical applications of a large polarized mercury pool electrode were investigated. The polarographic waves obtained have distinct current maxima whose heights vary in a linear fashion with the concentration of the reducible ion. The half-peak potentials are independent of concentration and correspond, within 0.05 volt, to the half-wave potentials associated with the dropping mercury electrode. Thallous, lead, copper, cadmium, zinc, bismuth, and indium ions have been studied. The polarized pool electrode has been found to be applicable to the determination of ions at lower concentrations than the more conventional polarographic methods, while retaining many of the advantages of the dropping electrode. The currents are proportional to concentration, the ions can be identified by their reduction potentials, and the electrode has a high hydrogen overvoltage. The area of the electrode can be varied over wide limits, the charging current density is much smaller, and conventional equipment can be used. The polarograms obtained are theoretically predictable within 5% by the equations applicable to oscillographic polarography.

THE polarographic determination of electroactive substances by the dropping mercury electrode and various solid microelectrodes has been extensively investigated. Although a great variety of electrodes have been developed, the use of a stationary, polarized mercury pool to perform similar determinations has not received attention in application to analytical polarography. Arthur (*1*) has recently worked with a stationary mercury drop and stirred solutions, and Lee has developed a rotating mercury electrode (*5*). Zlotowski (*9*) in connection with work on overvoltage used a mercury pool electrode to investigate polarization phenomena.

The main objectives of this paper were to study the characteristics of the mercury pool electrode, to evaluate it as an analytical tool, and to compare it with the more common dropping mercury electrode. The studies were limited to electrode processes involving reduction of an ion to an amalgam. It was believed that the more important factors to consider in such a work should include the magnitude and reproducibility of the residual current, the linearity of the polarograms with concentration, the sensitivity of the electrode as compared to the dropping mercury electrode, the usefulness of the half-wave potentials in the qualitative identification of ions, the influence of the rate of potential scanning, the effect of previously discharged metals, and the effect of surface active agents.

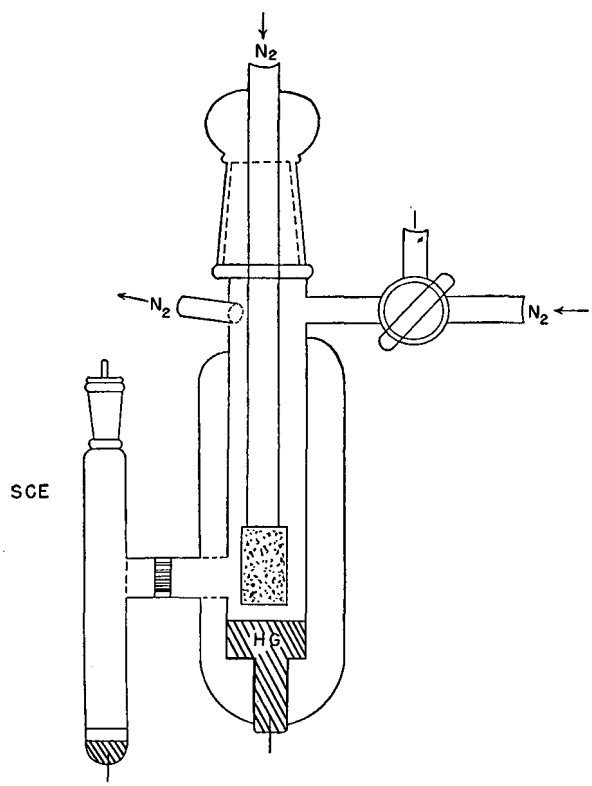


Figure 1. Diagram of Cell

From an initial evaluation of the problem it seemed that the mercury pool should have a high hydrogen overvoltage and possess a fluid and reproducible surface. It would have the advantage of a large area for the electrode surface, and should, therefore, be useful in the range of concentrations lower than those determinable by the dropping mercury electrode. This area could be conveniently varied over a wide range as dictated by the particular problem at hand. One of the serious limitations to the use of the dropping mercury electrode is the comparatively large charging currents associated with the continuous flow of mercury. By using a stationary pool the magnitude of the charging current density should be greatly decreased. On the other hand, the mercury pool would not have a surface which is renewable during the recording of a polarogram.

It would appear that the mercury pool electrode might be useful in studies involving derivative and oscillographic polarography. In both cases the serious difficulties associated with the fluctuations of the dropping mercury might be overcome.

APPARATUS AND MATERIALS

The cell used for this work is illustrated in Figure 1. It consisted, essentially, of a water-jacketed borosilicate glass tube 2.0 cm. in diameter fused to a borosilicate glass tip 1.0 cm. in diameter. The over-all length of the tube and tip was about 13 cm.

The area of the mercury surface was calculated as 2.86 sq. cm. on the assumption that the surface of the pool could be represented as the zone of a sphere. The cell could contain from 10 to 20 ml. of the solution to be determined. A platinum wire sealed into the bottom of the tip provided the electrical connection to the mercury pool.

The entire inner glass surface of this chamber was treated with Desicote (Beckman Instrument Co.) to prevent the wetting of the glass surface by the aqueous solutions below the surface of the

mercury. This was done in order to maintain a constant mercury-solution interface and more reproducible currents.

The reference electrode incorporated into the cell was a saturated calomel electrode isolated by means of a sintered-glass disk and agar plug.

The nitrogen necessary to remove dissolved oxygen in solutions was Air Reduction Co.'s Seaford nitrogen (99.99% with a hydrogen impurity). It was not further purified before use but, after saturation with water vapor, was introduced into the solution through a fritted-glass cylinder leading directly into the center of the solution chamber and connected through the head of the cell to the three-way stopcock and bypass. The distance between the surface of the mercury pool and this sintered-glass cylinder was about 0.5 cm.

Ten to 20 minutes' passage of nitrogen sufficed to decrease the dissolved oxygen in the solution to a negligible value. During the actual determinations, the nitrogen was bypassed by means of the three-way stopcock over the surface of the solution. All connections in the nitrogen inlet system were of Tygon tubing. The gas leaving the apparatus was passed through a bubbler to prevent back-diffusion of air into the cell.

Commercially available triple-distilled mercury was occasionally found to contain traces of oil, and unless this was removed, current transients were obtained during the recording of the polarograms. Although these transients did not affect the height of the waves obtained, they could be eliminated by dispensing the mercury from a dry, grease-free buret in which it had been allowed to stand at least 24 hours, or alternatively by passing the mercury through a sintered-glass disk before use.

The entire electrolysis compartment was water-jacketed to permit the circulation of constant-temperature water (25.0° ± 0.1° C.) and it was found necessary to mount the weighted stand supporting the cell on a sponge rubber cushion to protect the pool from shocks and vibrations.

A modified commercial model recording polarograph, the Leeds and Northrup Electrochemograph, was used for this work. The polarizer unit in this instrument was found to give troublesome fluctuations in the recorded polarograms caused by the rather coarse helical winding of the polarizing slide-wire. It was replaced by a ten-turn helipot having roughly five times as many turns and the fluctuations were thus greatly decreased. The polarizing voltage was obtained from dry cells with suitable resistances in series to drop 1 to 3 volts across the helipot. The voltage drop across the slide-wire was checked with a potentiometer. The rate of rotation of the helipot was varied by means of a Georrell and Georrell synchronous motor containing variable-speed gears, so that the mercury pool could be polarized at different rates. It was possible, using this apparatus, to run a polarogram over a 1-volt range at a rate of 50 mv. per second to 1 mv. per hour. Appropriate gears were obtained, so that the recorder chart could be driven at a rate corresponding to 100 mv. per inch.

All solutions were prepared by the dilution of 0.01 M stock solutions prepared from reagent grade chemicals and analyzed by conventional procedures. The salts used were zinc chloride, lead acetate, copper nitrate, cadmium chloride, thallium nitrate, bismuth nitrate, and indium chloride. Dilutions were carried out with double-distilled water and enough potassium nitrate solution to make all solutions 0.01 M in respect to potassium nitrate. The bismuth salt was dissolved in sulfuric acid and the solutions were diluted so that the final concentration of the sulfuric acid was 0.5 M.

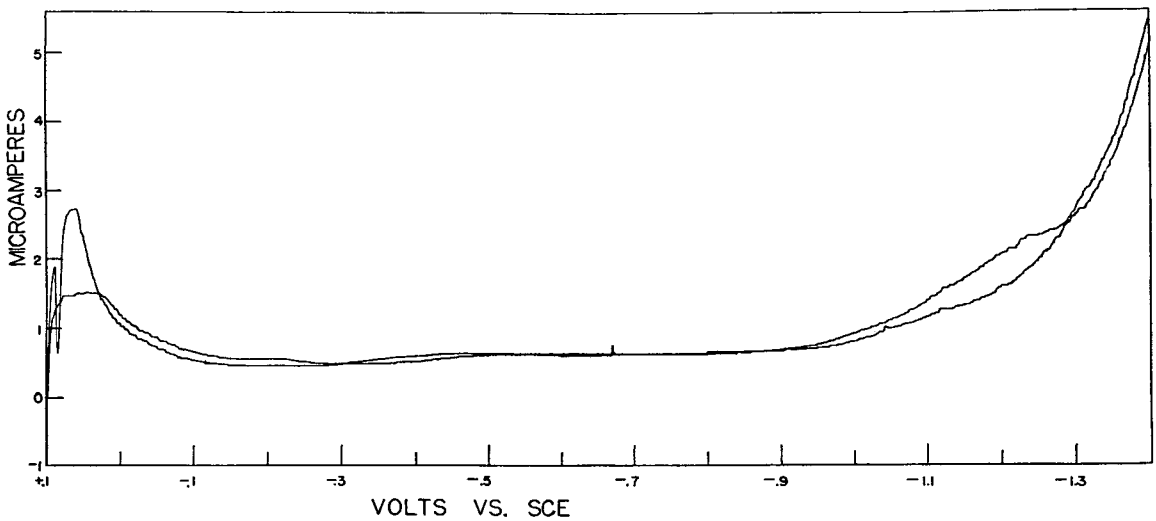


Figure 2. Reproducibility of Residual Current

The polarograms were obtained by placing 10 ml. of appropriate solution in the cell, deaerating for 10 minutes, adding 5 ml. of triple-distilled mercury, and deaerating with nitrogen for an additional 10 minutes. After bypassing the nitrogen over the surface of the solution, the electrode was polarized at the desired rate.

Reproducibility of background was determined on 0.01 M solutions of potassium nitrate, the salt used as the supporting electrolyte for most of the determinations. Variation of current with concentration was determined by obtaining polarograms of solutions containing from 5×10^{-6} to 10^{-4} M concentrations of the reducible ions.

Comparison polarograms carried out with the dropping mercury electrode utilized 10^{-4} M solutions with no maximum suppressor, since at the concentrations used, no maximum appeared.

RESIDUAL CURRENT

The magnitude of the residual current of an electrode used in polarographic work is determined by the presence of traces of electroreducible substances and the charging current. With the dropping mercury electrode, the charging current is greatly increased by the fact that the mercury is continuously flowing. With a stationary mercury pool, the magnitude of the charging current density should be greatly decreased, as was found to be the case.

In Figure 2 the residual current associated with the mercury pool electrode is shown. Two runs made on different solutions at different times show the reproducibility that can be expected in such work.

Although the absolute values of the currents measured with the mercury pool are somewhat greater than the dropping mercury electrode, the area of this electrode is about 75 times greater, so the actual current density is considerably smaller. The contribution to the residual current by traces of reducible material is usually not serious with the dropping mercury electrode be-

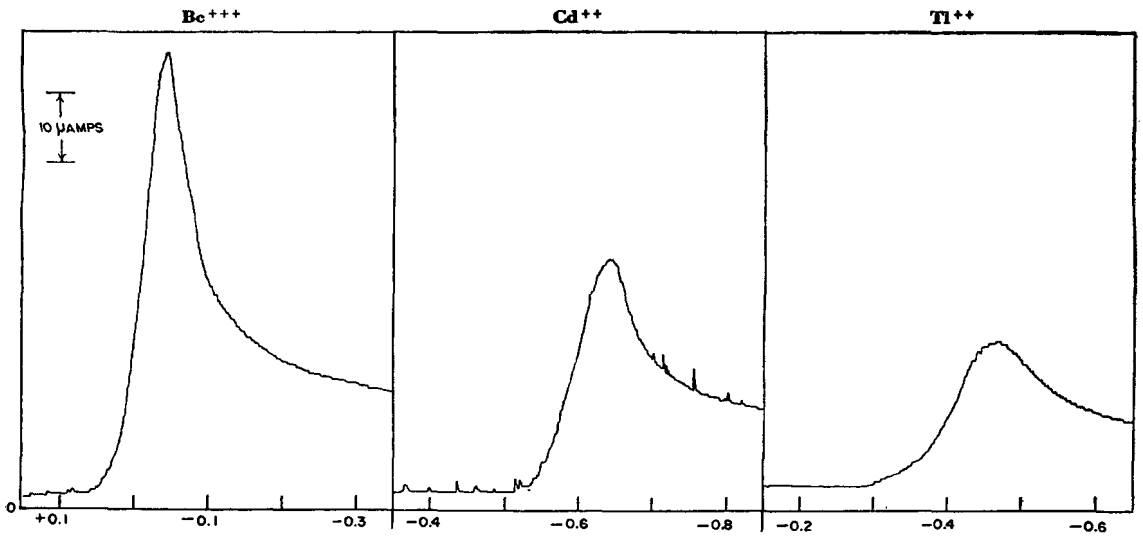


Figure 3. Wave Variation with Ionic Change

Solutions $10^{-4}M$
Left. Bi^{+++} *Center.* Cd^{++} *Right.* Tl^{+}

cause of the relatively greater contribution of the charging current. In the case of the pool electrode, however, with its increased sensitivity and decreased charging current density, this problem is more severe. Care must be taken in handling the supporting electrolyte solutions to prevent contamination in the analysis of the dilute solutions. In one of the polarograms in Figure 2 a small wave appears at 1.0 volt in one run but not in the other. This is believed to be a contamination caused by zinc. That the major contribution to the residual current of the mercury pool is due to impurities in the supporting electrolyte can be surmised from the actual shape of the polarogram. The curve has a much smaller slope than that obtained with the dropping mercury electrode, indicating that the relative contribution to the curve by impurities is high as compared to the charging current. This flatter shape of the polarograms is advantageous experimentally. It is easier to compensate these polarograms than those of the dropping mercury electrode with their considerably greater slope.

Although the two polarograms shown in Figure 2 are probably not as reproducible as those obtained with the conventional dropping electrode, this is caused by the greater sensitivity of the mercury pool and the greater likelihood of contamination. With the recorder sensitivity used in the analysis of solutions more concentrated than 5×10^{-5} M, the residual currents are reproducible within the accuracy of the recorder.

The small peak at the beginning of the polarogram is similar to that obtained with amalgam electrodes (*2*) and is possibly caused by formation of a trace of some insoluble mercury salt at the more positive potentials.

LINEARITY AND REPRODUCIBILITY OF POLAROGRAMS

The shape of the polarograms obtained with the mercury pool electrode differs considerably from conventional polarographic waves, as can be seen in Figure 3. The shape of the wave changes with the number of electrons involved in the reduction of the ion. The pronounced current peaks differ from the maxima obtained with the dropping mercury electrode, and are caused by the fact that the voltage change is more rapid than the rate at which the diffusion layer is set up. This is a dynamic equilibrium depending on the rate of polarization, and entirely different curves would be obtained by the use of a manual polarograph.

In contrast to the usual polarographic maxima, the peak

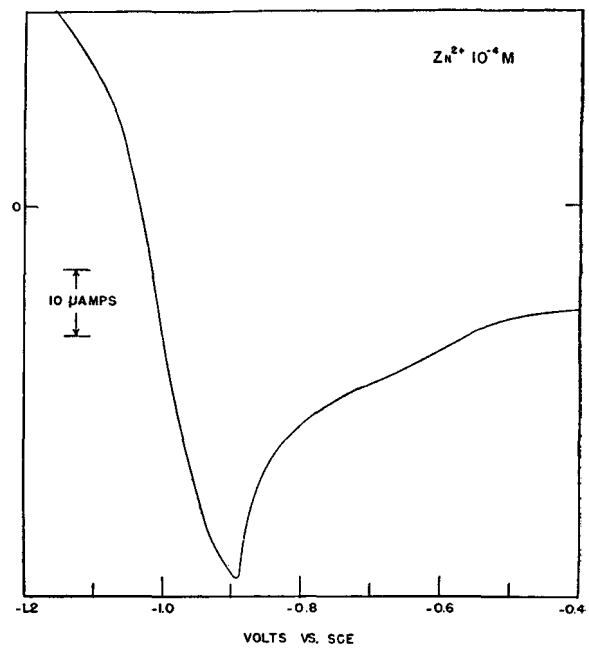


Figure 4. Reverse Scan of Pool Electrode

heights of the current-voltage curves are linear with the concentration of the ions being reduced. These data are shown in Table I. The reproducibility of the current peaks run on the same solution is about 4%. The values for the zinc ion reduction consistently showed the poorest reproducibility of the various ions tried.

Two possible procedures can be used in correcting for the contribution of the residual current to the recorded polarogram. One is by recording a background current and subtracting the appropriate current value, and the other is by extrapolation of the base line preceding the polarographic reduction curves. In the concentration range greater than 5×10^{-5} either method can be used with equivalent accuracy. With more dilute solutions, the latter procedure was found to be desirable because of the greater sensitivity of the electrode to traces of electroreducible substances.

Table I. Variation of Current Maximum with Concentration for Various Ions Using Mercury Pool Electrode

Supporting electrolyte, 0.01 M KNO_3
t = 25° C.
Scanning rate, 200 mv./minute

Ion	i_{max}/C, Ampere/Mole/Liter, When C Is: 5×10^{-6}	10^{-5}	5×10^{-5}	10^{-4}	Av. max./C	% Deviation Max.	% Deviation Av.
Tl^+	0.204	0.210	0.210	0.196	0.205	4.4	2.4
Pb^{++}	0.300	0.320	0.336	0.309	0.316	6.3	3.8
Cd^{++}	0.334	0.354	0.334	0.300	0.331	9.3	4.5
Cu^{++}	0.260	0.240	0.272	0.257	0.256	6.2	3.5
Zn^{++}	0.360	0.350	0.350	0.315	0.344	8.5	6.1
Bi^{+++}[a]	0.660	0.620	0.620	0.610	0.628	5.1	2.6

[a] Supporting electrolyte 0.5 M H_2SO_4.

If the voltage on the pool is scanned from more negative to less negative values, the polarograms are different, as would be expected. Figure 4 shows a curve of this type. Similar phenomena are obtained in oscillographic polarography. A valley is obtained rather than a peak, caused by anodic dissolution of the metal which has been deposited at the more negative voltages. The curve is approximately the same shape as that obtained from forward polarization but is inverted and reversed. No correlations of these current voltage curves with ion concentrations were attempted.

SENSITIVITY OF MERCURY POOL ELECTRODE

As the purpose of this study was to extend the range of polarographic methods to more dilute solutions, a comparison of the sensitivity of the mercury pool electrode and the dropping mercury electrode is presented in Table II.

Table II. Current Values and Half-Wave Potentials Obtained at Mercury Pool and Dropping Mercury Electrodes[a]

Concentration, 10^{-4} M
t = 25° C.
Supporting electrolyte, 10^{-2} M KNO_3
Scanning rate, 200 mv./minute

Ion	Mercury Pool Cathode i_{max}, μa.	Mercury Pool Cathode $\frac{1}{2}$ peak, volts	Dropping Mercury Electrode i_d, μa.	Dropping Mercury Electrode $\frac{1}{2}$ wave
Tl^+	19.4 ± 0.1	−0.46	0.82	−0.43
Pb^{++}	31.0 ± 0.1	−0.42	1.05	−0.38
Cd^{++}	30.0 ± 0.0	−0.61	1.00	−0.56
Cu^{++}	25.7 ± 1	−0.01	0.92	+0.03
Zn^{++}	31.5 ± 0.5	−1.03	0.87	−0.99
Bi^{+++}[b]	61.0 ± 2	−0.01	1.60	−0.02

[a] $m^{2/3}t^{1/6}$ = 2.63 at zero applied potential.
[b] Supporting electrolyte 0.5 M H_2SO_4.

These data list only a comparison of the magnitude of the currents obtained by both methods. What is probably more significant is the ratio of the measured currents to the residual current. In the case of 10^{-4} M zinc solution, this ratio for the mercury pool is 24.0, while for the dropping mercury electrode it is only 2.3.

The range of concentrations studied was 10^{-4} to 5×10^{-6} M. However, more dilute solutions can be determined if the accuracy desired is less critical. Peaks can be identified to about 5×10^{-7} M.

Although the area of the mercury pool is about 75 times as large as the dropping mercury electrode used in these comparisons, the current values obtained are only 25 to 40 times greater, depending on the specific ion involved. This is probably caused by a thicker diffusion layer at the mercury pool. With a dropping mercury electrode of 3 seconds' drop time, the diffusion layer is still comparatively thin. With the pool electrode, the time lag between the point at which reduction becomes appreciable and the current peak is much greater. This allows a longer diffusion path to be set up, resulting in lower current density. By increasing the voltage scanning rate, the diffusion layer can be decreased and the peak currents increased.

USEFULNESS AND CONSTANCY OF HALF-PEAK POTENTIALS

The fact that the half-wave potentials obtained with the dropping mercury electrode are independent of concentration is a valuable asset in identifying the substances being reduced. With the mercury pool electrode, it was found that the voltage at which the current peak was obtained varied slightly, and in a roughly linear fashion, with concentration. However, with all metals except copper the half-peak potential (the potential of the wave at one half the current maximum) was found to be independent of concentration over the range 10^{-4} to 5×10^{-6} M. The half-peak potential of copper varied from +0.03 to −0.01 volt versus the saturated calomel electrode for a concentration change from 5×10^{-6} to 10^{-4} M. The half-peak potential agreed well with the half-wave potential obtained with the dropping mercury electrode in the same solution, as can be seen in Table II.

EFFECT OF PREVIOUSLY DISCHARGED METALS ON POLAROGRAMS

The effect of the previous discharge of lead ion upon the height of the zinc wave is illustrated in Table III. Solutions of 8.3×10^{-6} M zinc ion in a supporting electrolyte of approximately 0.2 M potassium acetate containing varying amounts of lead,

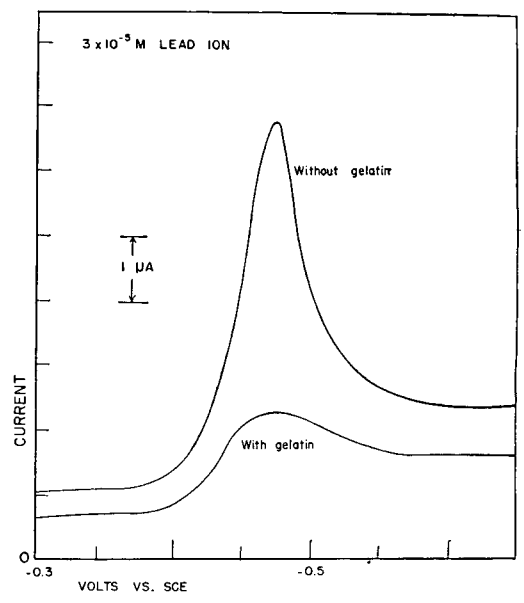


Figure 5. Effect of Gelatin on Lead Wave

Table III. Determination of Zinc in Presence of Lead by Mercury Pool Electrode

Scanning rate, 100 mv./minute
t = 25° C.
Supporting electrolyte, 0.2 M $KOAc$

Concn. of Zn^{++}, $M \times 10^6$	Concn. of Pb^{++}, $M \times 10^6$	Wave Height, μa. Zn^{++}	Wave Height, μa. Pb^{++}
8.3	0.00	1.90 ± 0.05	0.00
8.3	4.17	1.82 ± 0.06	0.82 ± 0.02
8.3	8.33	1.80 ± 0.05	1.72 ± 0.02
8.3	16.6	2.00 ± 0.05	4.46 ± 0.02
8.3	166	1.60 ± 0.02	54.5

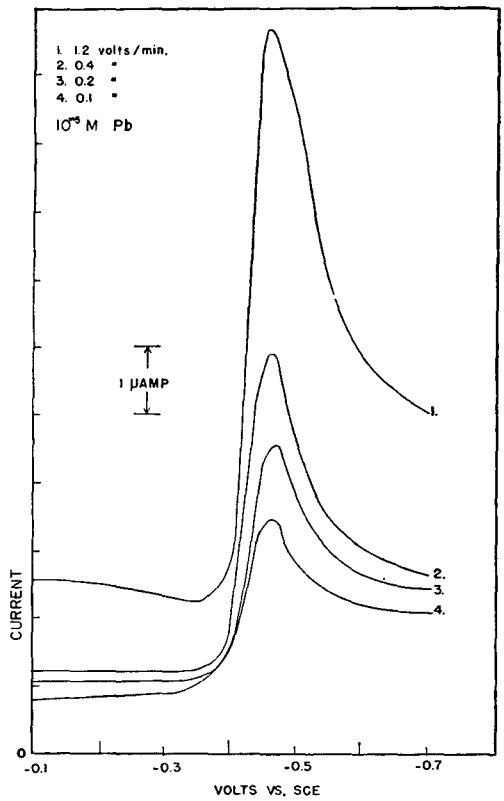


Figure 6. Influence of Scanning Rate on Shape of Polarograms

were analyzed for both lead and zinc content. The scanning rate was 100 mv. per minute. As can be seen, a lead content of one half to twice as much zinc had little effect on the wave height of the zinc. As the lead concentration increased to 20 times the zinc concentration, the accuracy involved in measuring the small greatly compensated zinc wave decreased.

INFLUENCE OF SURFACE ACTIVE AGENTS

The effect of gelatin upon the lead wave was also studied. The supporting electrolyte was 0.2 *M* potassium acetate and the polarization rate 100 mv. per minute. Maxima are usually observed in the automatic recording of polarograms using stationary solid electrodes. This type of maxima is not removed by the addition of surface active agents (*7*). With the polarized pool electrode the lead maximum could be greatly reduced by the addition of gelatin, but was not entirely eliminated by the amount of gelatin used. The half-peak potential was not affected. An illustration of the behavior of the lead wave with and without gelatin is shown in Figure 5.

THEORETICAL ASPECTS

The polarograms obtained at the mercury pool cathode are similar to the type which are found by oscillographic procedures employing the dropping mercury electrode. The electrolytic process involved in both cases is fundamentally the same. Using oscillographic techniques the polarizing voltage is scanned across the drop so rapidly that the electrode can be considered to be stationary. The only difference seems to be the rate at which the potential change is applied. Current peaks are obtained in both cases as the result of the reduction of ions near the surface of the electrode, the establishment of a diffusion layer, and the subsequent thickening of this layer with time. The increase in the length of the diffusion path accounts for the decrease in the reduction current, resulting in a current maximum. Because of the similarity of both processes, an attempt was made to apply the equations developed for oscillographic polarography to the mercury pool cathode.

Randles (*6*) has derived an expression for the height of an oscillographic recorded polarogram for an ion-amalgam reversible reduction. This derivation was based on the diffusion of ions to a plane surface and adapted to the dropping mercury electrode, where the surface area is expressed as $r^{2/3}t^{2/3}$. If area is resubstituted for the functions involving the dropping mercury electrode, the expression is:

$$i_{max} = \frac{0.216\sqrt{2}FAn^{3/2}v^{1/2}D^{1/2}C}{(0.0118)^{1/2}10^3} \quad (1)$$

in which F is the faraday, A is the area in square centimeters, n is the number of electrons involved in the reduction of the ion, V is the voltage scanning rate in volts per second, D is the diffusion coefficient, and C is the concentration in moles per liter. Combining constants, the equation becomes:

$$i_{max} = 192\sqrt{2}\,A\,n^{3/2}v^{1/2}D^{1/2}C \quad (2)$$

Sevcik (*8*) has also derived an expression for the wave height in oscillographic polarography:

$$i_{max} = 0.361nFACD^{1/2}\left(\frac{nFv}{RT}\right)^{1/2} \quad (3)$$

where R and T have their usual significance and C is expressed in moles per milliliter. Again on combining constants and dividing through by 1000 so that concentration may be expressed in moles per liter, the equation becomes:

$$i_{max} = 217\,A\,n^{3/2}v^{1/2}D^{1/2}C \quad (4)$$

where

A = electrode area, square centimeters
n = number of electrons involved in reduction
v = rate of voltage scanning, volts per second
D = diffusion coefficient of ion, square centimeters per second
C = concentration, moles per liter

As Delahay (*3*) has pointed out, the equations are then identical except for the value of the numerical constant.

Both Randles and Delahay have tested their data from oscillographic methods against the Randles equation. Randles obtained excellent agreement for thallous, lead, and cadmium ion, poorer agreement for manganous and zinc ion. Delahay obtained good agreement for thallous ion, poorer agreement for lead and cadmium. However, he used much faster voltage scanning rates in his work. He concluded from these results and from the departure from linearity of i_{max} with square root of the scanning rate, that the cadmium reduction is not truly reversible, a fact apparent only through oscillographic techniques.

The effect of each of the factors in the above equation on the magnitude of the current peak has been evaluated. The contribution of the diffusion coefficient and the number of electrons transferred cannot be checked separately. However, the value of $i_{max}/D^{1/2}$ should be in the ratio 1:2.83:5.20 for ions having electron changes of 1, 2, and 3, respectively. If the value for $i_{max}/D^{1/2}$ is divided by the $^3/_2$ power of the electron change, a constant value should be obtained for all ions, provided that the concentration, electrode area, and scanning rate are not changed.

The values of the diffusion coefficients recorded for ions at infinite dilution are not particularly applicable to this work. Since the diffusion coefficient is related to the ionic species present, its value was determined, under the same conditions in which they were used, by polarographic procedures. The corrected form of the Ilkovič equation (*4*) was used to calculate these coefficients.

The study of the effect of rate of polarization upon wave height and curve shape is illustrated in Figure 6. The data are shown in Table IV for a solution 10^{-5} *M* in lead ion. The proportionality

Table IV. Variation of Wave Height with Scanning Rate

Ion, 10^{-6} M Pb^{++}
t = 25° C.
Supporting electrolyte, 0.01 M KNO_3

Scanning rate, Volts/Min.	i_{max}, μa.	(Scanning Rate)$^{1/2}$ (Volt/Sec)$^{1/2}$	$\frac{i_{max}}{V^{1/2}}$
0.1	2.50	0.0408	61.2
0.2	3.50	0.0577	60.6
0.4	4.90	0.0816	60.0
1.2	9.00	0.141	63.6
		Av.	61.3 ± 1.1

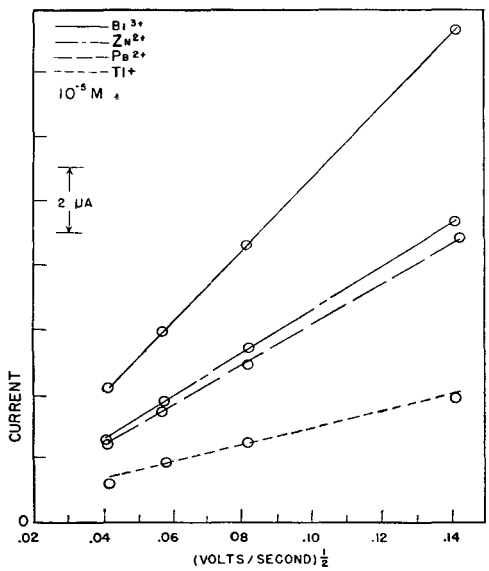


Figure 7. Relation of Current to Square Root of Rate of Polarization

of peak height *vs.* scanning rate for other ions is shown in Figure 7. In agreement with the work of Rogers *et al.* (*7*) on polarography using solid platinum electrodes, the height of the maxima was found to increase with increasing rate of polarization. The half-peak potential of the lead reduction was independent of scanning rate, remaining at −0.42 ± 0.01 volt. This fact also agrees with the work of Rogers, who found the half-peak potential to be independent of scanning rate for platinum electrodes. If the relative magnitude of the residual current can be kept small, the relative increase in peak height with more rapid scanning rates will obviously heighten the sensitivity.

Ions which undergo three-electron reductions such as bismuth show higher, sharper peaks than those which undergo two- or one-electron reductions. The height of the maxima is, of course, also dependent upon the diffusion coefficient if other factors are the same.

The cadmium polarogram is typical of the two-electron reductions but zinc and copper show somewhat broadened peaks. Indium failed to give a wave similar to that of bismuth, but instead showed a wave flattened at the top and without a sharp peak. The failure of this ion to follow normal behavior may be caused by the slow dissociation of complex chloride ions limiting the rate of electrode reaction. For this reason the data for indium have not been included in this paper, as its behavior does not appear to be at all predictable by the equations under consideration.

A summary of $i_d/cm^{2/3}t^{1/6}$ values, diffusion coefficients, and the quotient $\frac{i_{max}}{D^{1/2}n^{3/2}}$ are given in Table V. It can be seen that the values for $\frac{i_{max}}{D^{1/2}n^{3/2}}$ are approximately constant. The average value is 3.56×10^3 with a mean deviation of about 5%. The diffusion coefficients given here can be considered to apply only to the cases under study. From the above data a proportionality constant was calculated corresponding to the value of $192\sqrt{2}$ of the Randles equation (*6*) and 217 for the Sevcik equation (*8*). The values for each of the variables was substituted in the equation

$$k = m\frac{i_{max}}{An^{3/2}D^{1/2}v^{1/2}C} \qquad (5)$$

The calculated constant, k, derived for each ion, is shown in Table V. The average value of 218 is in good agreement with that derived by Sevcik. In the cases of zinc and copper, which show the largest deviations, the reaction does not appear to be reversible from the shape of the polarograms. A comparison of peak current heights, predicted by the Sevcik equation, and those obtained experimentally, can be seen in Figure 8.

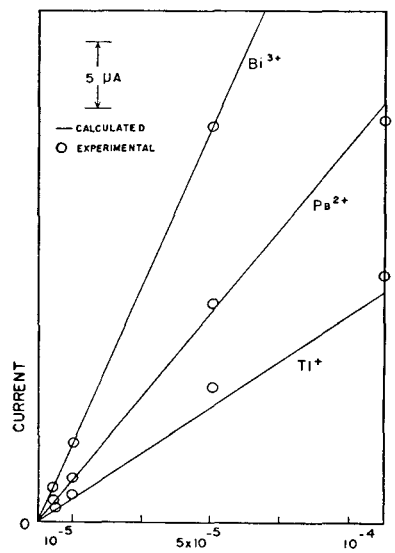


Figure 8. Comparison of Experimental Values and Those Calculated from Sevcik Equation

Table V. Effect of Diffusion Coefficient and Electron Change on Peak Heights

Concn., 10^{-4} M
t = 25° C.

Ion	$\frac{i_d}{Cm^{2/3}t^{1/6}}$, DME	Diffusion Coefficient Calcd. from DME	$\frac{i_{max}}{D^{1/2}n^{3/2}}$	k^a
Tl^+	3.12	2.57×10^{-5}	3.82×10^{-3}	232
Pb^{++}	3.99	1.06	3.38	204
Cd^{++}	3.80	0.96	3.43	207
Cu^{++}	3.50	0.80	3.31	195
Zn^{++}	3.31	0.71	3.88	254
Bi^{+++}	6.08	1.09	3.55	216

[a] Average value of k = 218 ± 16.

ACKNOWLEDGMENT

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Tabulated Diffraction Data for Hexagonal Isomorphs

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To extend the systematic identification of crystalline compounds by isomorphism beyond the cubic system and tetragonal system, the authors have tabulated 117 hexagonal prototype structures, arranged 1287 hexagonal substances according to the ascending order of their axial ratios, and obtained representative powder diffraction patterns for 53 hexagonal structures. These data are useful for verifying standard powder patterns and for identifying solids by x-ray diffraction methods.

CHEMICAL identification of crystalline compounds by isomorphism depends for its applicability on a systematic arrangement of the representative diffraction patterns of the various known crystal structures. The tabulations of the cubic structures (*6*) and the tetragonal structures (*8*) have proved useful in the phase identification of solids when the requisite powder diffraction standards are not found in the literature. The utility of this method has now been extended to the hexagonal system. The procedure for comparing diffraction patterns of isomorphous substances has been described previously (*7*); hence only the tabulated diffraction data for hexagonal isomorphs are reported in this paper.

Figures 1 to 6 exhibit 53 representative powder diffraction diagrams corresponding to 53 hexagonal structures. The diagrams are designated as in the "Strukturbericht" (*5, 9–12*) and are arranged in sets starting with the A-structures pertaining to elements and ending with the O-structures for organic compounds. Within each set the simplest structure with the highest symmetry is listed first. The averaged relative intensities, based on the Dow file of standards, refer to Debye-Scherrer-Hull patterns taken with filtered MoKα radiation and with filtered CuKα radiation corrected for θ dependence. The variations in relative intensities to be expected are illustrated in Table I. For each structure only reflections compatible with its hexagonal space group are shown. Some 25 compounds were synthesized and their powder diffraction patterns carefully indexed in order to obtain more representative relative intensities for those structures for which only two or three isomorphs had been studied.

GENERAL PROCEDURE FOR IDENTIFYING NONCATALOGUED PATTERN

1. Using the log d scale at bottom of Figure 1, plot the log d values and corresponding relative intensities of the unidentified pattern on a narrow strip of paper.
2. Verify that the pattern is noncubic (*6*).
3. Find an isomorphic prototype among the representative diffraction patterns for the anisotropic crystal structures.
4. Compute the lattice constants and check the appropriate classification tables (for the hexagonal system refer to Tables IV and V).
5. Confirm the identification of the unknown phase by a qualitative spectroscopic analysis or by chemical tests.

The following example illustrates the procedure. Columns 1 and 2 of Table II list the diffraction data of a water-soluble white powder submitted for analysis. To establish if the sample is multicomponent, a 50-mg. portion of the fine powder was leached in a 0.3-ml. test tube with approximately 0.05 ml. of distilled water. The slushy crystal mass was stirred with a fine Nichrome wire, and approximately 0.02 ml. of solution was removed with a micro eyedropper, the tip of which was covered with a small piece of cotton. The solid obtained from the evaporated drop of filtrate was examined by x-ray powder diffraction and identified as potassium bromide. A semiquantitative spectroscopic analysis of the original powder showed 10 to 25% potassium and listed the following trace impurities: sodium, aluminum, calcium, silica (0.1 to 0.3%); iron, magnesium, copper (0.01 to 0.1%).

As the unidentified powder lines of the original sample could not be matched with published x-ray powder diffraction standards, an attempt was made to establish isomorphism with one of the standard crystal structures. After plotting the log d values of the first 20 unidentified lines on a strip of paper and marking the stronger lines, one begins with the cubic system and finds that no satisfactory match can be found with the stronger lines unless one assumes several cubic phases with lattice constants greater than 10 A. Proceeding to the tetragonal system, one finds an approximate match for ten lines out of the first seventeen at $c/a = 1.23$, $a = 6.31$ A., and $c = 7.74$ A. However, no substance is listed for these lattice constants (*8*). Another approximate fit is located at $c/a = 1.17$, $a = 8.45$ A., and $c = 9.85$ A. No tetragonal substance with these lattice constants is listed, and again one is left with unindexed lines. In neither case can an approximate intensity match be found with any of the 40 representative diffraction patterns for tetragonal structures (*8*).

To index all the unidentified powder lines in the tetragonal system would require unreasonably large lattice constants. It is very probable, however, that the unidentified powder lines pertain to a single phase, because the relative intensities of these lines (referred to the 4.91 A. spacing as the strongest line) do not vary appreciably in the following three patterns: original sample, undissolved part from water leach, and recrystallized sample of undissolved part. Examination of the original sample under the polarizing microscope revealed that the powder is too finely subdivided for phase identification. However, recrystallization from water produced sufficiently large crystals to establish the presence of a uniaxial phase. Using the same log d strip as for the tetragonal system, one attempts to index the unidentified lines on the hexagonal patterns of Figures 1 to 6.

A systematic way of finding a prototype structure is to match successively the strongest line of the unidentified phase against the first, second, or third most intense line of the representative patterns. Then one follows the same procedure with the second strongest line and, if necessary, the third line. The first reasonable fit with the data is noted for the β_1-$\mathbf{K_2UF_6}$ structure with $c/a \approx 0.65$ ($a \approx 9.8$ A. and $c \approx 6.3$ A). However, the intensity agreement is not satisfactory. Under structure β_1-$\mathbf{K_2UF_6}$ in Table IV no compounds are listed with $c/a = 0.65$. Structure $\mathbf{K1_1}$ permits ready indexing of all the lines at $c/a = 0.64$ ($a = 9.80$ A., $c = 6.29$ A.) and matches the relative intensities well. Searching under $\mathbf{K1_1}$ for $c/a = 0.64$, one tentatively identifies the unknown as $K_2S_2O_6$. On heating a few milligrams of the original powder above 300° C. on a platinum crucible top to convert the dithionate to sulfate and sulfur dioxide, one obtains a strong sulfate test on the acidified residue. The addition of barium chloride reagent to a water solution of the original powder gave

(*Continued on page 1716*)

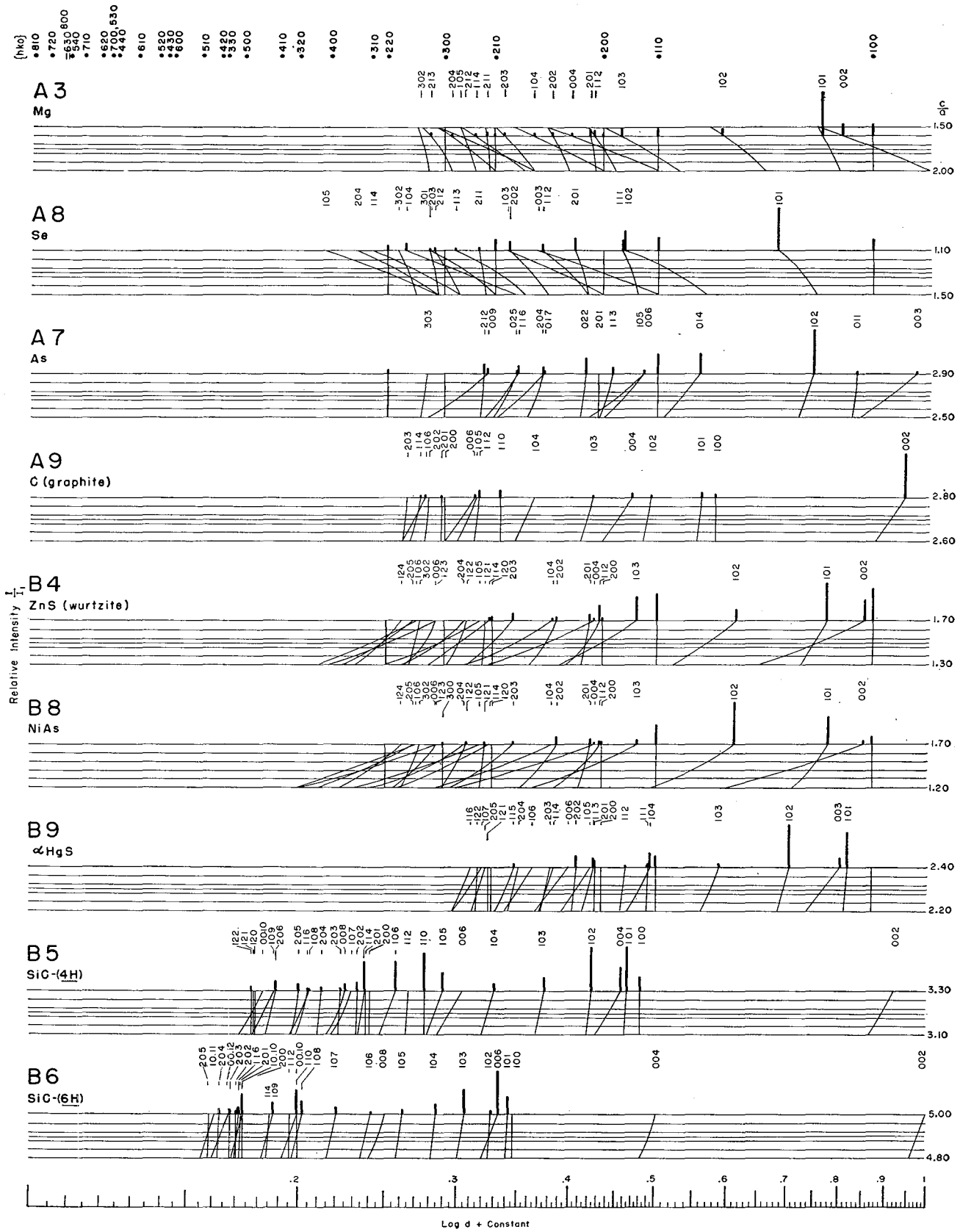


Figure 1. Representative Diffraction Patterns of Hexagonal Structures

The log d_{hk0} values of the various structures (Figures 1 to 6) are aligned according to the {*hko*} reflections at the top of each figure. (To conserve printing space some of the structures are translated to the left—e.g., **A9, B5, B6.** For these cases the {*hko*} reflections are labeled.) The change of d_{hkl} with *c/a* is expressed graphically (*4, 13*) and covers the *c/a* spread encountered within the particular isomorphous group.

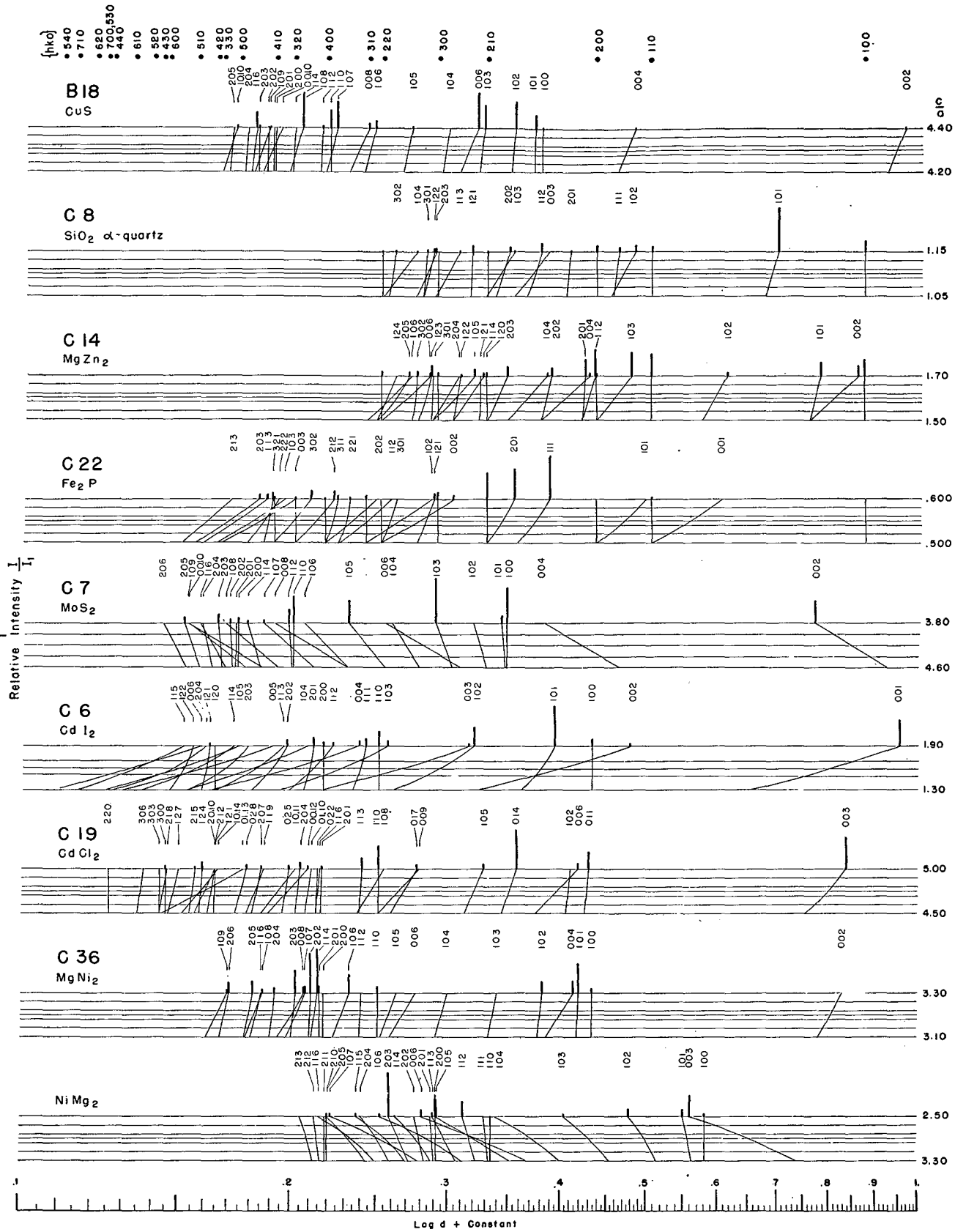


Figure 2. Representative Diffraction Patterns of Hexagonal Structures

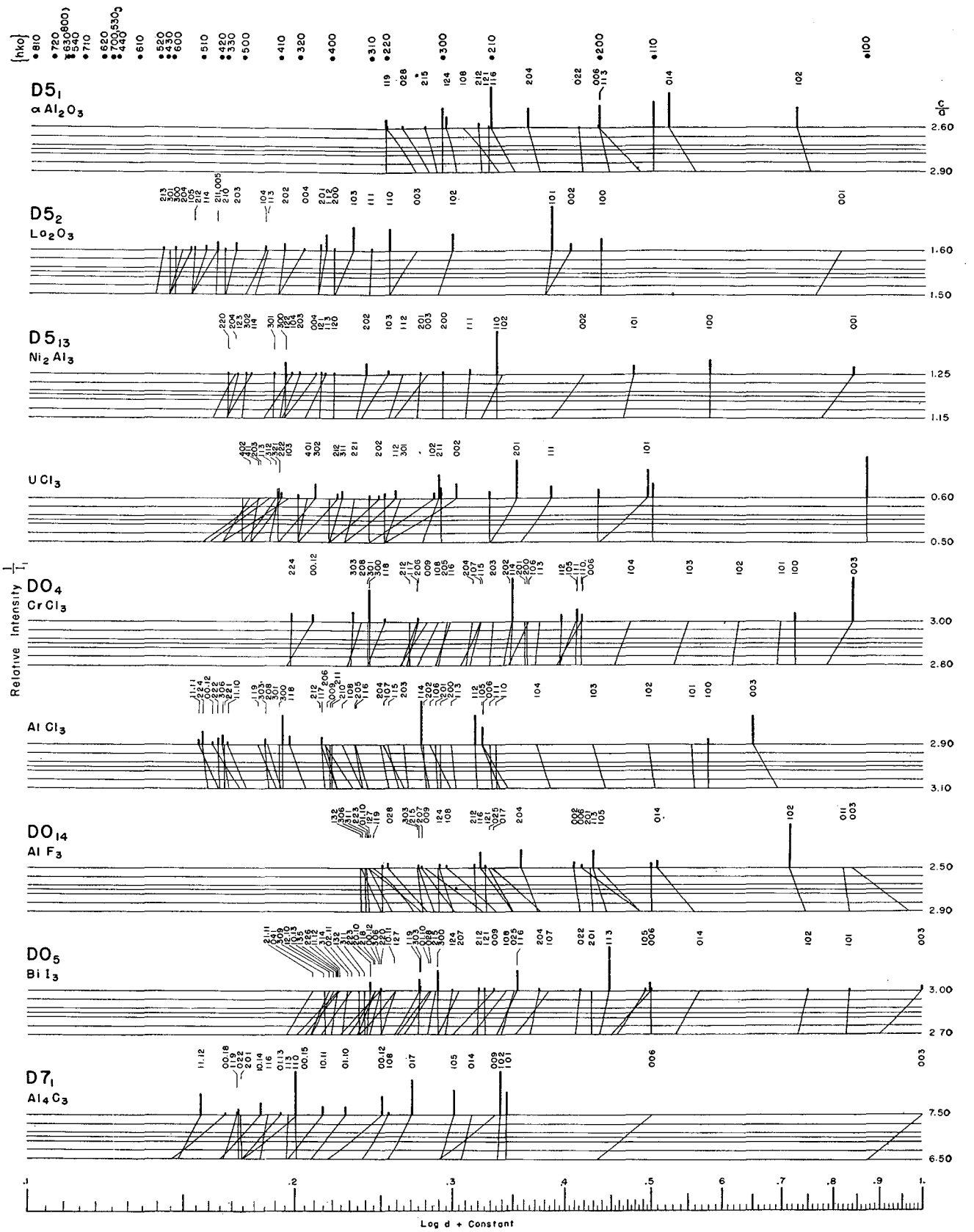


Figure 3. Representative Diffraction Patterns of Hexagonal Structures

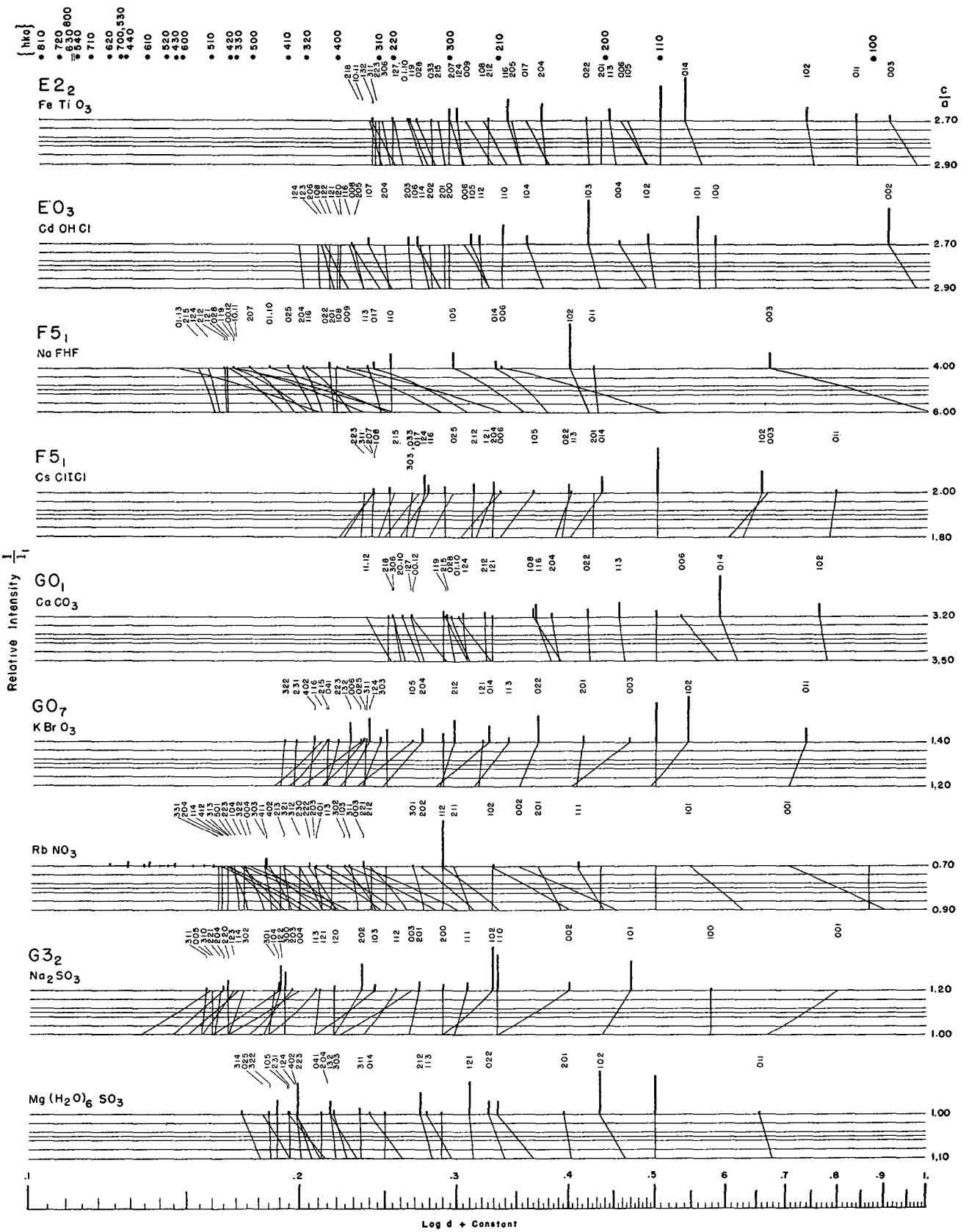


Figure 4. Representative Diffraction Patterns of Hexagonal Structures

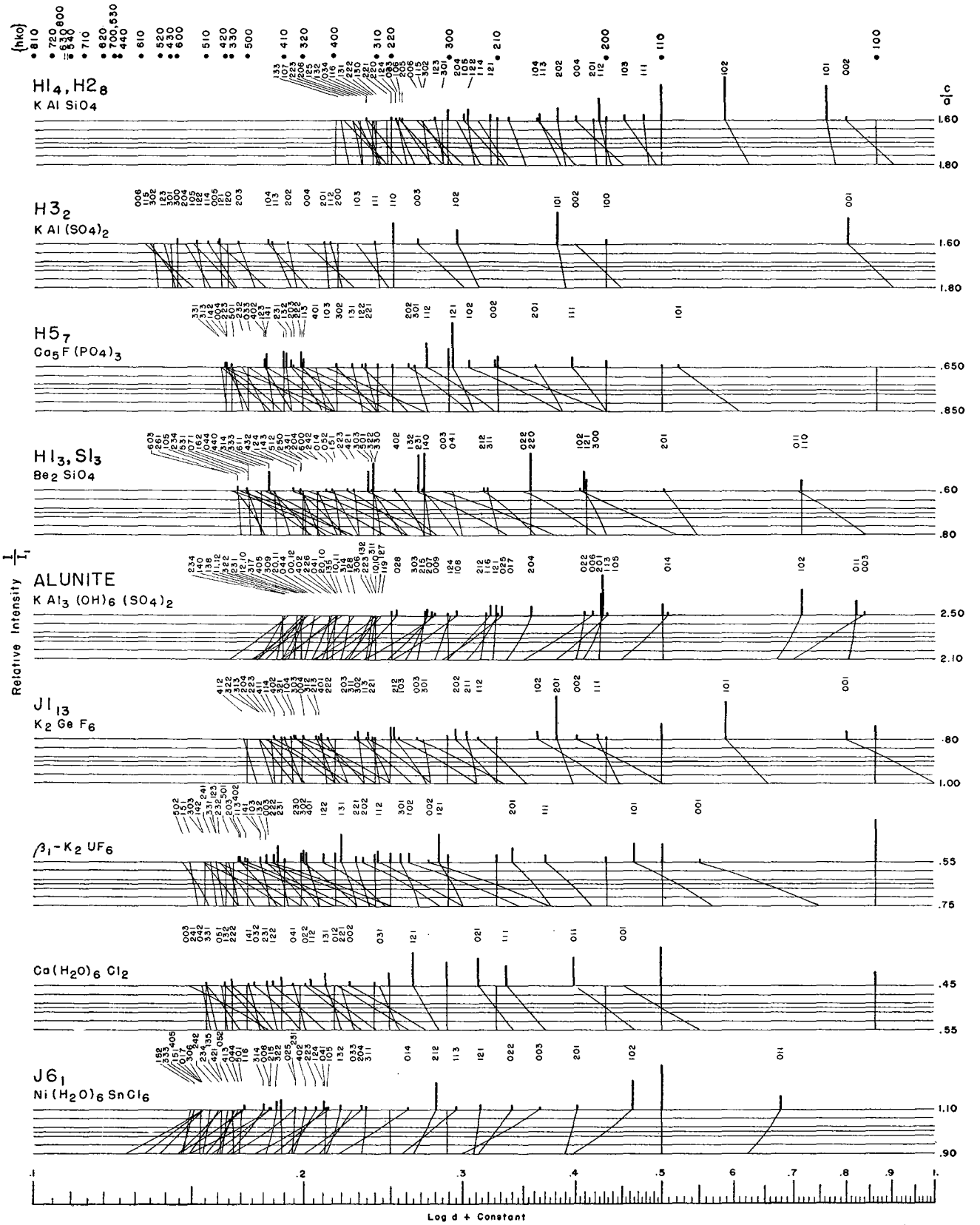


Figure 5. Representative Diffraction Patterns of Hexagonal Structures

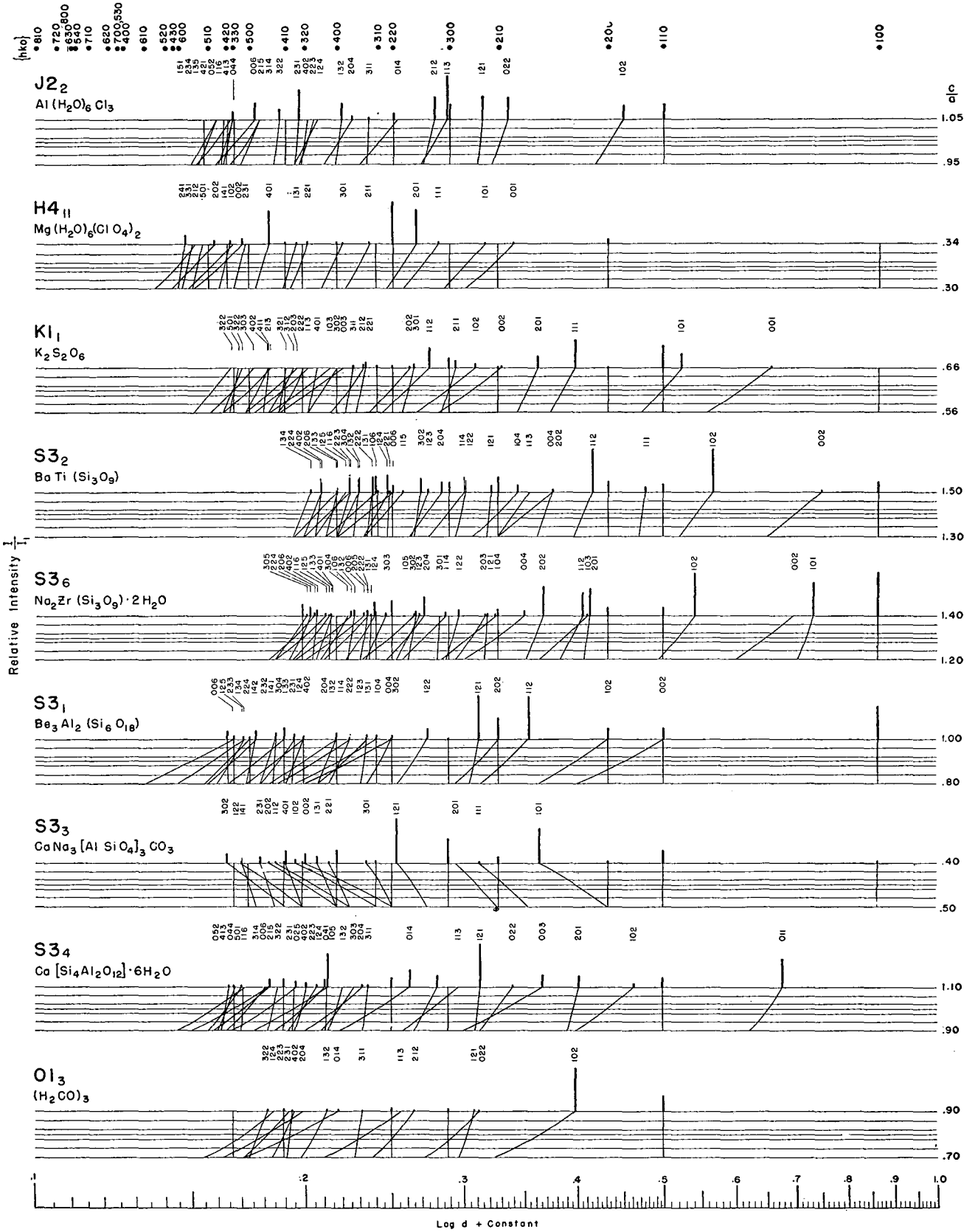


Figure 6. Representative Diffraction Patterns of Hexagonal Structures

Table I. Representative Powder Diffraction Pattern for Structure C6 Compared with Specific Powder Patterns

Relative intensities of the powder pattern for structure C6 represent the arithmetically averaged relative intensities of 11 members of this isomorphous group of 61 substances (see Table IV).

	I/I_1					
		$Mg(OH)_2$		$Cd(OH)_2$		$TiCl_2$ (I),
{hkl}	C6	MoKα	CuKα	MoKα	CuKα	CuKα
001	0.59	0.53	0.50	1.00	0.50	0.25
002	0.05	...	...	...	...	0.06
100	0.14	...	0.03	0.63	1.00	...
101	0.92	1.00	1.00	1.00	1.00	1.00
102	0.43	0.40	0.27	0.40	0.27	0.42
003	...	...	...	...	...	...
103	0.10	0.13	0.10	...	...	0.19
110	0.35	0.33	0.27	0.30	0.42	0.29
111	0.17	0.17	0.13	0.30	0.30	0.06
004	0.08	0.03	0.04	0.07	...	0.04
112	0.04	...	...	0.20	0.10	...
200	0.08	...	...	0.13	0.10	...
201	0.16	...	...	0.20	0.17	0.09
104	0.01	...	0.01	...	...	...
202	0.11	0.04	0.05	0.15	0.07	0.08
113	0.01	...	...	...	...	0.03
005	...	...	...	...	...	...
203	0.01	...	...	0.03	...	0.06
105	...	...	...	...	...	0.03
114	0.05	...	...	...	...	0.07
120	0.02	...	...	0.08	0.10	...
121	0.06	0.04	0.04	0.13	0.10	0.07

Table II. X-Ray Powder Diffraction Data

Filtered CuKα radiation was used to obtain the powder diffraction data. d = interplanar spacing. I = intensity in arbitrary units. {hkl} are indices for the various reflections. The lattice constant for the cubic phase (preferentially soluble phase) is a = 6.592 ± 0.005 A.; for the hexagonal phase, a = 9.80 A. and c = 6.29 A.

Original Sample		Soluble Phase		{hkl} Hexagonal phase	{hkl} Soluble phase	
d, A.	I	d, A.	I			$(I/I_1)_{hex.}$
6.30	1	...	...	001	...	0.01
5.10	2	...	...	101	...	0.03
4.91	75	...	...	110	...	1.00
3.87	75	...	...	111	...	1.00
3.81	15	3.82	75	...	111	...
3.51	25	...	...	201	...	0.33
3.30	350	3.30	>350	...	200	...
2.95	25	...	...	102	...	0.33
2.84	20	...	...	211	...	0.27
2.82	40	...	...	300	...	0.53
2.65	50	...	...	112	...	0.67
2.57	4	...	...	301	...	0.05
2.52	4	...	...	202	...	0.05
2.33	150	2.33	>350	...	220	...
2.27	12.5	...	...	221	...	0.17
2.24	12.5	...	...	212	...	0.17
2.19	7	...	...	311	...	0.09
2.10	12.5	...	...	302	...	0.17
				003		
2.03	12.5	...	...	103	...	0.17
1.984	17.5	1.985	62.5	...	311	...
1.924	10	...	...	222	...	0.13
				113		
1.903	30	1.904	150	...	222	...
1.854	12.5	...	...	321	...	0.17
				410		
1.773	4	...	...	411	...	0.05
1.753	4	...	...	213	...	0.05
				402		
1.650	20	1.648	100	...	400	...
1.630	8	...	...	330	...	0.11
1.593	6	...	...	223	...	0.08
				412		
1.562	6	...	...	313	...	0.08
1.514	9	1.513	30	...	331	...
1.493	6	...	...	402	...	0.08
				501		
				114		
1.472	62.5	1.473	250	...	420	...
1.424	10	...	...	323	...	0.13
				422		
1.409	10	...	...	600	...	0.13
				214		
1.384	4	...	...	413	...	0.05
				601		
1.372	4	...	...	512	...	0.05
				304		
1.355	3	...	...	520	...	0.04
				431		
1.344	40	1.343	125	...	422	...
1.318	2	...	...	503	...	0.03
				224		
1.305	4	...	...	314	...	0.05
1.268	10	1.269	20	...	511	....
					333	
1.242	3	...	...	105	...	0.04
				522		
1.218	5	...	...	115	...	0.07
				324		

Table II. X-Ray Powder Diffraction Data (*Contd.*)

Original Sample		Soluble Phase		{hkl} Hexagonal phase	{hkl} Soluble phase	
d, A.	I	d, A.	I			$(I/I_1)_{hex.}$
1.186	3	...	...	701	...	0.04
				531		
1.162	10	1.164	25	...	440	...
1.120	3	...	...	225	...	0.04
				424		
1.112	3	1.113	12.5	...	531	...
1.096	30	1.097	50	...	600	...
				...	442	
1.041	20	1.042	20	434	620	...
				415		
				106		
				801		
0.992	15	0.993	25	...	622	...

Table III. Statistical Data on Tabulated Hexagonal Substances

Dominant structures	C6 B8 A3 $H5_7$ Cl4 UCl_3 $J6_1$ B4 $D0_6$
N_T = number of examples	61 56 47 46 31 23 21 20 20
Configurations favoring hexagonal symmetry	Octahedral, spherical, tetrahedral, trigonal prismatic, centro-triangular, 3n-cyclic
Prevalence of P lattices	72%
Prevalence of R lattices	28%
$\bar{n}_{hko}$ = average number of observed prism reflections per powder pattern	3.8; $1 \leq \bar{n}_{hko} \leq 8$
$\bar{\nu}_{hko}$ = probability of observing {hko}	($\bar{\nu}_{100}$, $\bar{\nu}_{110}$, $\bar{\nu}_{200}$, $\bar{\nu}_{210}$, $\bar{\nu}_{300}$, $\bar{\nu}_{220}$) = (0.57 0.91, 0.42, 0.40, 0.64, 0.53)
$\frac{\bar{I}_{hko}}{\bar{I}_1}$ = average relative intensity of {hko}	$\left(\frac{\bar{I}_{100}}{\bar{I}_1}, \frac{\bar{I}_{110}}{\bar{I}_1}, \frac{\bar{I}_{300}}{\bar{I}_1}\right)$ = (0.25, 0.41, 0.15)
$\bar{\nu}_n${hkl} = probability that {hkl} is nth strongest powder reflection of hexagonal structure	$\bar{\nu}_1$ {102, 101, 110} = (0.23, 0.15, 0.06) $\bar{\nu}_2$ {110, 102, 101} = (0.17, 0.09, 0.08) $\bar{\nu}_3$ {110, 101, 102} = (0.25, 0.08, 0.04)
Most probable axial ratio, c/a	1.6; $0.13 \leq c/a \leq 71.1$

Table IV. Hexagonal Substances Tabulated by Types

Table IV lists 117 hexagonal prototype structures, including some pseudo-hexagonal cases such as $AlCl_3$, $RbNO_3$, and $Mg(ClO_4)_2.6H_2O$. For each isomorphous type the members are arranged in the ascending order of their axial ratios. If two members have the same value for c/a, the one with the smaller lattice constants is listed first. (To avoid repetition the various literature values have been averaged.) For specific references see literature citations (*2, 3, 5, 9–12, 14, 16–19*). All kX values have been converted to A.

c/a	a, A.	c, A.	Substance
		A3	
1.55–1.56	2.76–2.77	4.30	$Cu_{1-x}Zn_{3+x}$
1.58	2.29	3.61	α-Be
1.58	3.52	5.57	Lu
1.58	3.54	5.60	Er
1.58	3.56	5.63	Ho
1.58	3.59	5.66	Dy
1.58	3.60	5.67	Tb
1.59	2.70	4.28	Ru
1.59	2.72	4.32	Os
1.59	3.21	5.09	Hf
1.59	3.23	5.15	α-Zr
1.59	3.31	5.25	Sc
1.59	3.53	5.57	Tm
1.59	3.63	5.76	Gd
1.59	3.65	5.81	Y
1.60	2.74	4.39	Tc
1.60	2.95	4.70	Ti
1.60	3.45	5.52	Tl
1.61	2.76	4.46	Re
1.61	2.80	4.49	$Fe_{1-x}Zn_{7+x}$
1.61	3.67	5.89	Nd
1.62	2.51	4.07	β-Co
1.62–1.63	3.19–3.10	5.16–5.04	Mg-Cd (80-42 at. % Mg)
1.62	3.20	5.18	δ-(Mg, Ag) (3 at. % Ag)
1.62–1.63	3.20–3.21	5.19–5.21	Mg-Zn (3-0 at. % Zn)
1.62	3.66	5.91	Pr
1.62	3.66	5.94	β-Ce
1.62	3.75	6.07	α-La
1.63	2.65	4.33	(Ni)
1.63	2.73	4.43	β-Cr
1.63	3.07–3.10	4.99–5.04	$MgCd_{3-x}$

Table IV. Hexagonal Substances Tabulated by Types (*Continued*)

c/a	a, A.	c, A.	Substance
		A3 (*Contd.*)	
1.63	3.13	5.09	$Cd(Mg, Al)_2$
1.63	3.21–3.17	5.21–5.15	Mg-Al (2-11 at. % Al)
1.63	3.21	5.20	Mg-Mn (1.5 at. % Mn)
1.63	3.21	5.21	Mg
1.63	3.58	5.84	He (1.45° K., 37 atm.)
1.63	3.76	6.13	H_2 (4° K.)
1.63	4.32	7.06	β-Sr (521° K.)
1.64	3.97	6.50	β-Ca
1.64	4.04	6.62	β-N_2 (~40° K.)
1.86	2.67	4.95	Zn
1.86	2.67	4.96	Zn-Cd (1 at. % Cd)
1.86	2.67	4.97–4.98	Zn-Al (0-5.0 at. % Al)
1.87–	2.67–	4.97–4.99	Hg-Zn (1.51-5.87 at. % Hg)
1.89	2.98	5.62	Cd
		A7	
2.61	4.55	11.86	Bi
2.62	4.30	11.28	Sb
2.80	3.77	10.56	As
2.89	3.77	10.89	As-Sn (70.9 at. % As)
		A8	
1.14	4.35	4.96	Se
1.33	4.46	5.92	Te
		A9	
2.74	2.46	6.75	C (graphite)
		A10	
1.94	3.48	6.74	Hg (177° K.)
		B4	
1.60	2.90	4.62	CuH
1.60	3.12	4.99	AlN
1.60	3.26	5.21	ZnO
1.60	3.26	5.23	(Zn, Cd)O (5 mole % CdO)
1.60	3.28	5.26	(Zn, Mn)O (22 mole % MnO)
1.60	4.40	7.03	NH_4F
1.61	3.54	5.70	InN
1.62	3.06	4.95	TaN
1.62	3.98	6.44	MnS
1.62	4.15	6.72	CdS
1.62	4.53	7.36	MgTe
1.63	2.70	4.38	BeO
1.63	3.19	5.18	GaN
1.63	4.13	6.73	MnSe
1.63	4.20	6.86	Cd(S, Se)
1.63	4.31	7.03	CdSe
1.64	3.82	6.25	ZnS
1.64	4.06	6.66	CuBr (664–743° K.)
1.64	4.59	7.52	AgI
1.65	4.31	7.09	CuI (675–713° K.)
		B5	
3.27	3.08	10.08	SiC-(*4H*)
3.27	3.81	12.45	ZnS-(*4H*)
		B6	
4.90	3.08	15.12	SiC-(*6H*)
4.90	3.82	18.71	ZnS-(*6H*)
		B7	
12.23	3.83	46.84	ZnS-(*15R*)
12.28	3.08	37.82	SiC-(*15R*)
		B8	
1.21	4.20	5.10	CuSn
1.23	4.18–4.19	5.13–5.16	$NiIn_{1-x}$
1.23	4.23	5.21	γ-FeSn (~44 at. % Sn)
1.23	4.28	5.25	$CuIn_{1-x}$
1.24–1.25	4.40–4.38	5.47–5.49	$MnSn_{1-x}$
1.25	4.04	5.03	$FeGe_{1-x}$
1.26	4.05–4.15	5.12–5.21	$CoSn_{1-x}$
1.26	4.03–4.11	5.14–5.18	$FeSb_{1-x}$
1.26–1.27	4.15–4.05	5.21–5.12	$NiSn_{1-x}$
1.28	3.93	5.01	$CoGe_{1-x}$
1.28–1.30	3.96–3.85	5.05–4.99	$NiGe_{1-x}$
1.28	4.25	5.46	PtPb
1.28	4.32	5.56	RhSn
1.28	4.35	5.55	AuSn
1.28	4.46–4.49	5.69–5.74	$PdPb_{1-x}$
1.29	4.38–4.40	5.63–5.66	$PdSn_{1-x}$
1.31	3.92	5.14	Ni(Sb, As)
1.31	3.94	5.15	NiSb
1.32	4.08	5.36	NiBi
1.32	4.11	5.44	PtSn
1.32	4.14	5.46	PtTe
1.33	4.12	5.48	CrSb
1.33	4.14	5.48	PtSb
1.34	3.88	5.19	CoSb
1.36	3.76	5.10	NiAs,NiSb
1.36	3.96	5.37	NiTe
1.37	4.08	5.59	PdSb
1.37	4.14	5.67	PdTe
1.38	3.90	5.37	CoTe
1.39	3.61–3.63	5.02–5.05	Ni(As, Sb)
1.40	3.62	5.05	NiAs
1.40	3.99	5.57	IrSn
1.40	4.13	5.79	MnSb
1.42	4.31	6.13	MnBi
1.46	3.62	5.29	CoSe
1.46	3.67	5.34	NiSe
1.49	3.81	5.66	FeTe
1.53	3.39	5.19	CoS
1.53	3.72	5.71	MnAs
1.55–1.56	3.42–3.43	5.32–5.34	β-NiS
1.56	3.98	6.21	CrTe
1.57	3.37	5.30	(Fe, Co)S
1.58	3.51	5.56	$Fe_{1-x}Se$
1.60	3.42	5.47	(Ni, Fe)S
1.61	3.80	6.12	VTe
1.62–1.63	3.60–3.69	5.82–6.03	$Cr_{1-x}Se$
1.62	4.13	6.71	MnTe
1.63	3.43	5.56	$Cr_{1-x}S$
1.63	3.63	5.92	FeSe
1.66–1.68	3.44–3.46	5.69–5.80	$Fe_{0.33-0.96}S$
1.66	3.45	5.71	CrS
1.67	3.59	5.99	VSe
1.67	3.83	6.39	TiTe
1.68	3.45	5.81	FeS
1.73	3.36	5.81	VS
1.75	3.56	6.22	TiSe
		B9	
2.29	4.16	9.52	HgS
		B12	
2.66	2.52	6.69	BN
		B13	
0.32	9.86	3.19	γ-NiSe
0.328–0.329	9.59–9.63	3.15–3.17	NiS
		B18	
4.32	3.79	16.38	CuS
4.38	3.94	17.25	CuSe
		B22	
1.94	5.39	10.45	RbSeH
1.99	5.15	10.24	KSeH
1.99	5.17	10.30	RbSH
2.01	4.96	9.95	KSH
2.05	4.47	9.16	NaSH
2.05	4.66	9.54	NaSeH
		B30	
1.61	10.68	17.19	MgZn
		B35	
0.807	5.28	4.26	CoSn
0.828	5.61	4.65	PtTl
0.839	5.30	4.45	β-FeSn
0.956	4.55	4.35	ε-InNi
		C6	
1.27	4.04	5.13	$PdTe_2$
1.30	4.02	5.21	$PtTe_2$
1.34	3.48	4.67	$Cd(OH)_2$
1.36	3.73	5.07	$PtSe_2$
1.37	3.41	4.67	$(Cd, Mn)(OH)_2$
1.37	3.86	5.29	$NiTe_2$
1.38	3.25	4.48	$Fe(OH)_2$
1.38	3.50–3.52	4.83–4.85	$(Ca, Cd)(OH)_2$
1.38	3.59	4.93	$Ca(OH)_2$
1.38–1.43	3.89–3.79	5.38–5.41	$CoTe_{2-x}$
1.40	3.59	5.01	$Cd(OH)_{1.6}Cl_{0.4}$
1.41	3.33	4.69	$Mn(OH)_2$
1.42	3.55	5.03	PtS_2
1.43	3.79	5.41	$CoTe_2$
1.46	3.19	4.65	$(Co, Zn)(OH)_2$
1.46	3.19	4.66	$Zn(OH)_2$
1.46	3.20	4.66	$Co(OH)_2$
1.47	3.14	4.62	$(Ni, Zn)(OH)_2$

Table IV. Hexagonal Substances Tabulated by Types (*Continued*)

c/a	a, A.	c, A.	Substance
		C6 (*Contd.*)	
1.47–1.49	3.17–3.12	4.66–4.64	$(Co, Ni)(OH)_2$
1.48	3.11	4.61	$Ni(OH)_2$
1.48	3.16	4.67	$(Co, Mg)(OH)_2$
1.48	3.16	4.67	$(Co, Zn)(OH)_2$
1.51	3.10	4.68	$(Ni, Mg)(OH)_2$
1.51	4.55	6.89	PbI_2
1.52	3.05	4.67	$(Ni, Zn)(OH)_2$
1.52	3.13	4.74	$Mg(OH)_2$
1.54	4.25	6.54	ZnI_2
1.55	3.59	5.55	$Cd(OH, Cl)_2$
1.55	4.49	6.97	CaI_2
1.55	4.49	6.97	YbI_2
1.59	3.69	5.86	ZrS_2
1.60	3.10	4.94	Ta_2C
1.61	3.65	5.88	SnS_2
1.61	4.26	6.86	CdI_2
1.62	3.83	6.20	$MnBr_2$
1.63	3.80	6.19	$ZrSe_2$
1.64	3.77	6.18	VBr_2
1.64	3.83	6.27	$MgBr_2$
1.64	4.14	6.80	GeI_2
1.64	4.17	6.83	MnI_2
1.65	3.56	5.88	$TiCl_2$
1.65	3.75	6.18	$FeBr_2$
1.66	3.70	6.13	$CoBr_2$
1.66	4.11	6.82	TiI_2
1.66	4.15	6.89	MgI_2
1.67	3.41	5.70	TiS_2
1.67	4.00	6.67	VI_2
1.67	4.05	6.76	FeI_2
1.68	3.97	6.66	CoI_2
1.69	3.54	5.99	$TiSe_2$
1.70	3.16	5.37	$Ni(OH)_{1.5}Cl_{0.5}$
1.71	3.23	5.51	$Co(OH)_{1.5}Cl_{0.5}$
1.71	3.28	5.60	$Co(OH)_{1.5}Br_{0.33}Cl_{0.17}$
1.73	3.41	5.91	TaS_2
1.73	3.77	6.51	$TiTe_2$
1.81	3.65	6.61	$Cd(OH)_{1.5}I_{0.5}$
1.83	3.24	5.92	$Co(OH)_{1.5}Br_{0.5}$
1.83	3.36	6.13	VSe_2
1.84	3.18	5.83	$Ni(OH)_{1.5}Br_{0.5}$
1.91	3.01	5.72	Ag_2F
2.19	3.18	6.97	$Co(OH)_{1.5}(NO_3)_{0.5}$
		C7	
3.90	3.16	12.32	MoS_2
3.90–3.92	3.16	12.29–12.34	$WS_{1.9-2.0}$
3.94	3.29	12.97	WSe_2
		C8	
1.10	(4.73)	(5.19)	BeF_2
1.10	4.91	5.40	α-SiO_2
1.11	5.04	(5.60)	$FePO_4$
1.12	4.90	(5.47)	$AlPO_4$
1.12	5.04	(5.62)	$AlAsO_4$
1.13	4.99	5.65	α-GeO_2
		C10	
1.63	4.51	7.35	H_2O (273° K.)
1.63	4.54	7.36	D_2O (272° K.)
1.63	5.04	8.24	SiO_2 (β-trydymite)
		C12	
7.85	3.89	30.53	$CaSi_2$
		C14	
1.61	6.64	10.66	$BaMg_2$
1.62	4.22	6.84	$FeBe_2$
1.62	6.23	10.12	$CaMg_2$
1.63	4.24	6.92	$MnBe_2$
1.63	4.26	6.96	$CrBe_2$
1.63	4.36	7.10	$ReBe_2$
1.63	4.40	7.14	VBe_2
1.63	4.78	7.81	$TeFe_2$
1.63	4.81	7.86	$TaFe_2$
1.63	4.83	7.88	$CbFe_2$
1.63	4.87	7.95	$TaMn_2$
(1.63)	4.96	8.08 × 2	$TiMn_2$
1.63	5.14	8.39	$ZrCr_2$
1.63	5.26	8.60	$ZrRe_2$
1.63	5.48	8.95	$ThMn_2$
1.63	6.43	10.47	$SrMg_2$
1.64	4.44	7.29	$MoBe_2$
1.64	4.45	7.28	WBe_2
1.64–1.65	4.87–4.82	7.81–7.97	$Mg(Ni, Cu)_2$
1.64	4.87	7.97	$CbMn_2$
1.64	5.01	7.89	$MgCu_{1.6}Si_{0.5}$
1.64	5.04	8.24	$ZrMn_2$
1.64	5.10	8.36	$MgCuAl$-$MgCu_2$
1.64–1.65	5.14–5.22	8.44–8.62	$Mg(Zn, Cu)_2$
1.64	5.17	8.51	$MgZn_2$
1.64	5.19	8.53	$ZrOs_2$
1.64	5.28	8.66	ZrV_2
1.64	6.26	10.25	$CaLi_2$
1.64	7.50	12.29	KNa_2
1.65	5.20–5.22	8.60–8.62	$Mg(Zn, Ni)_2$
1.66	5.14	8.51	$ZrRu_2$
		C19	
4.41	4.28	18.23	Cs_2O
4.54	3.86	17.50	$CdCl_2$
4.59	3.60	16.53	$Cd(OH)_{1.25}Cl_{0.75}$
4.71	3.78	17.82	$ZnCl_2$
4.75	3.69	17.51	$MnCl_2$
4.76	3.96	18.80	$CdBr_2$
4.78	3.93	18.77	$ZnBr_2$
4.90	3.55	17.36	$NiCl_2$
4.90	3.56	17.44	$CoCl_2$
4.90	3.58	17.55	$FeCl_2$
4.90	3.59	17.58	$Cd(OH)_{1.4}Br_{0.6}$
4.90	3.60	17.63	$MgCl_2$
4.93	3.73	18.34	$NiBr_2$
5.04	3.91	19.67	NiI_2
		C22	
0.511	6.77	3.46	Pd_2Ge
0.526	6.75	3.55	Pt_2Ge
0.532	6.49	3.45	Pd_2Si
0.567	6.09	3.46	Mn_2P
0.575	5.86	3.37	Ni_2P
0.583	5.85	3.41	$(Ni, Cu)_2P$
0.589	5.87	3.46	Fe_2P
		C27	
3.22	4.25	13.70	CdI_2
3.22–4.71	4.25–3.99	13.70–18.78	$Cd(Br, I)_2$
		C32	
0.647	4.99	3.23	UHg_2
1.00	4.28	4.28	$PrGa_2$
1.00	4.31	4.31	$CeGa_2$
1.00	4.32	4.32	$CaGa_2$
1.02	3.00	3.06	VB_2
1.02	3.05	3.11	MoB_2
1.02	4.33	4.40	$LaGa_2$
1.05	3.09	3.24	TaB_2
1.05	3.86	4.07	β-USi_2
1.07	3.03	3.23	TiB_2
1.07	3.09	3.31	CbB_2
1.08	3.01	3.25	AlB_2
1.11	3.17	3.53	ZrB_2
		C33	
6.95	4.32	30.07	Bi_2Te_2S
6.96	4.37	30.42	Bi_2Te_3
		C36	
3.26	4.73	15.40	$CoTi_2$
3.26	4.73	15.42	$TaCo_2$
3.26	4.74	15.46	$CbCo_2$
3.26	4.96	16.15	$ZrFe_2$
3.29	4.82	15.86	$MgNi_2$
3.30	4.82–4.87	15.94–16.10	$Mg(Ni, Zn)_2$
3.30	5.10	16.80	$MgCuAl$
		C40	
1.44	4.43	6.36	$CrSi_2$
		C41	
1.63	4.73	7.73	Fe_2W
		$D0_4$	
2.90	5.99	17.38	$CrCl_2$
		$D0_5$	
2.75	7.50	20.65	BiI_3
2.79	6.39	17.82	$ScCl_3$
2.79	7.50	20.93	SbI_3
2.86	6.13	17.54	$TiCl_3$
2.87	6.05	17.38	$FeCl_3$
2.87	6.42	18.40	$FeBr_3$
2.88	6.46	18.64	$TiBr_3$
2.89	6.02	17.38	VCl_3
2.91	6.29	18.30	$CrBr_3$
2.97	7.19	21.38	AsI_3
		$D0_6$	
1.02	6.99	7.16	SmF_3
1.02	7.07	7.23	PrF_3
1.02	7.12	7.28	CeF_3
1.02	7.13	7.29	$(Ce, La)F_3$
1.02	7.14	7.29	$(La, Ce, Pr)F_3$
1.02	7.17	7.34	LaF_3
1.03	7.03	7.21	NdF_3
1.75 × $\sqrt{3}$	4.20 × $\sqrt{3}$	7.41	$Pb_{0.5}Th_{0.5}F_2$
1.75	4.28	7.48	$Ba_{0.5}U_{0.5}F_2$
1.76	4.19	7.35	$Pb_{0.5}U_{0.5}F_2$
1.76	4.28	7.54	AcF_3

Table IV. Hexagonal Substances Tabulated by Types (*Continued*)

c/a	a, A.	c, A.	Substance
		$D0_6$ (*Contd.*)	
1.76	4.29	7.54	$Ba_{0.5}Th_{0.5}F_3$
1.77	4.09	7.25	PuF_3
1.77	4.12	7.29	NpF_3
1.77	4.14	7.34	UF_3
1.78	4.04	7.19	$Ca_{0.5}Th_{0.5}F_3$
1.78	4.08	7.24	AmF_3
1.78	4.11	7.30	$Sr_{0.5}U_{0.5}F_3$
1.78	4.14	7.34	$Sr_{0.5}Th_{0.5}F_3$
1.80	4.05	7.30	$ThOF_2$
		$D0_{12}$	
2.56	5.23	13.38	FeF_3
2.59	5.17	13.40	VF_3
2.62	5.07	13.30	CoF_3
2.79	4.89	13.65	RhF_3
2.81	5.06	14.22	PdF_3
		$D0_{14}$	
2.54	4.92	12.48	AlF_3
		$D0_{16}$	
(2.97)	(5.92)	(17.56)	$AlCl_3$
		$D0_{18}$	
1.77	4.27	7.60	Li_3P
1.77	4.71	8.33	Li_3Sb
1.77	4.99	8.82	Na_3P
1.77	5.10	9.00	Na_3As
1.77	5.37	9.52	Na_3Sb
1.77	5.46	9.68	Na_3Bi
1.77	5.79	10.24	K_3As
1.77	6.19	10.95	K_3Bi
1.78	4.40	7.83	Li_3As
1.78	4.87	8.65	Mg_3Hg
1.78	6.04	10.71	K_3Sb
1.78	6.04	10.72	$K_3(Sb, Te)$
1.82	4.64	8.46	Mg_3Au
		$D0_{19}$	
0.796	5.33	4.25	Ni_3In
0.799	5.46	4.36	Fe_3Sn
0.800–0.801	5.66–5.67	4.53–4.54	$Mn_{3+x}Sn_{1-x}$
0.802	5.29–5.31	4.24–4.26	$Ni_{3+x}Sn_{1-x}$
0.805	5.13	4.13	Co_3W
0.805	5.96	4.80	$Ti_3(Sb_{0.8}Ti_{0.2})$
0.809	6.28	5.08	Mg_3Cd
0.810	6.23	5.05	Cd_3Mg
0.817	5.35	4.38	$Mn_{3+x}Ge_{1-x}$
		$D0_{21}$	
1.02	6.99	7.13	Cu_3P
		$D0_{24}$	
1.63	5.11	8.32	Ni_3Ti
		UCl_3	
0.553	7.94	4.39	$PrBr_3$
0.554	7.93	4.39	$NpBr_3$
0.558	7.95	4.44	$CeBr_3$
0.559	7.94	4.44	UBr_3
0.563	6.27	3.53	$Dy(OH)_3$
0.565	6.25	3.53	$Er(OH)_3$
0.565	6.27	3.54	$Gd(OH)_3$
0.565	6.27	3.54	$Sm(OH)_3$
0.566	(6.24)	(3.53)	$Y(OH)_3$
0.566	7.97	4.51	$LaBr_3$
0.573	7.40	4.24	$NdCl_3$
0.574	7.40	4.25	$PuCl_3$
0.574	7.42	4.26	$PrCl_3$
0.576	7.38	4.25	$AmCl_3$
0.577	7.42	4.28	$NpCl_3$
0.579	7.45	4.31	$CeCl_3$
0.580	8.08	4.69	$AcBr_3$
0.581	6.48	3.77	$Pr(OH)_3$
0.581	7.44	4.32	UCl_3
0.583	6.43	3.75	$Nd(OH)_3$
0.585	7.48	4.38	$LaCl_3$
0.590	6.53	3.86	$La(OH)_3$
0.597	7.64	4.56	$AcCl_3$
		$D2_2$	
1.66	9.94	16.51	$MgZn_6$
		$D4_1$	
1.91	4.55	8.71	B_2H_6
		$D5_1$	
2.64	5.14	13.58	Ti_2O_3
2.71	4.96	13.42	α-Ga_2O_3
2.71	5.11	13.83	Rh_2O_3
2.73	4.79–4.99	13.09–13.64	$(Al, Fe)_2O_3$
2.73	4.76	13.00	α-Al_2O_3
2.74	4.98–5.01	13.65–13.71	$(Fe, Cr)_2O_3$
2.74	5.03	13.77	Fe_2O_3
2.75	4.78–4.93	13.08–13.55	$(Al, Cr)_2O_3$
2.75	4.95	13.61	Cr_2O_3
2.82	4.94	13.95	V_2O_3
		(See $E2_2$)	
		$D5_2$	
1.55	4.08	6.30	Ac_2O_3
1.56	3.85	6.02	Nd_2O_3
1.56	3.86	6.01	Pr_2O_3
1.56	3.89	6.07	Ce_2O_3
1.56	3.94	6.14	La_2O_3
1.58	4.58	7.24	Sb_2Mg_3
1.59	3.88	6.19	Th_2N_3
1.59	4.68	7.42	Bi_2Mg_3
		(See Ce_2O_2S)	
		$D5_6$	
4.00	5.93	23.73	$K_2O.11Fe_2O_3$
4.02	5.59	22.50	$Na_2O.11Al_2O_3$
4.03	5.93	22.88	$Rb_2O.11Fe_2O_3$
4.06	5.59	22.67	$(K, Na)_2O.11Al_2O_3$
4.06	5.59	22.72	$K_2O.11Al_2O_3$
		$D5_{13}$	
1.13	4.53	5.51	In_3Pt_2
1.18	4.40	5.25	In_3Ni_2
1.21	4.04	4.90	Al_3Ni_2
1.21	4.06	4.90	Ga_3Ni_2
1.21	4.53	5.50	In_3Pd_2
1.23	4.23	5.18	Ga_3Pt_2
		$D7_1$	
7.51	3.33	24.98	Al_4C_3
		$D8_5$	
5.41	4.74	25.63	Co_7W_6
5.41	4.75	25.68	Fe_7Mo_6
5.43–5.61	4.76–4.75	25.83–26.68	$Fe_{7+x}W_{6-x}$
		$D8_8$	
0.696	6.91	4.81	Mn_5Si_3
0.698	6.75	4.72	Fe_5Si_3
0.718	8.26	5.93	Mg_5Hg_3
		$D8_{10}$	
0.623	12.72	7.93	Cr_5Al_8
		$D8_{11}$	
0.992	7.68	7.61	Co_2Al_5
		Zn_5Ca	
0.779	5.43	4.23	Zn_5La
0.781	5.40	4.22	Zn_5Ca
0.796	4.96	3.95	Ni_5Ca
0.796	5.17	4.12	Cu_5La
0.800	5.10	4.08	Cu_5Ca
0.803	4.95	3.97	Ni_5Pr
0.804	5.14	4.13	$Cu_{5-x}Ce_{1+x}$
0.808	4.96	4.01	Ni_5La
0.811	4.91	3.98	Ni_5Gd
0.811	4.92	3.99	Ni_5Th
0.816	4.95	4.04	Co_5Th
0.818	4.96	4.06	Co_5Ce
0.822	4.87	4.00	Ni_5Ce
0.846	5.24	4.45	$Zn_{5+x}Th_{1-x}$
		$E0_2$	
2.81	3.67	10.29	$Cd(OH)Cl$
		$E2_2$	
2.70	5.12	13.85	$LiCbO_3$
2.74	5.05	13.85	$NiTiO_3$
2.76	5.05	13.93	$MgTiO_3$
2.76	5.09	14.06	$FeTiO_3$
2.77	5.05	13.72	$CoTiO_3$
2.80	5.14	14.36	$MnTiO_3$
2.82	4.96	13.98	$Fe_{1-x}Ti_{1+x}O$
2.84	5.26	14.94	$CdTiO_3$
3.00	5.33	15.98	$NaSbO_3$
3.40	5.30	18.25	$KSbO_3$
		(See $D5_1$)	
		$E2_3$	
0.943	5.48	5.17	$LiIO_3$
		$E9_2$	
1.63	5.43	8.85	$4BeO.NaSbO_3$
		$E9_4$	
6.59	3.29	21.64	Al_5C_3N
		$F0_2$	
0.945	6.21	5.87	OCS (<135° K.)

Table IV. Hexagonal Substances Tabulated by Types (*Continued*)

c/a	a, A.	c, A.	Substance
		$F4_1$	
2.46	6.46	15.92	$Fe_2(CO)_9$
		$F5_1$	
1.37	6.26	8.61	$AgFeO_2$
1.93	6.33	12.21	$CsICl_2$
4.05	3.68	14.88	$CaCN_2$
4.04	3.50	14.12	$NaHF_2$
4.18	3.64	15.20	NaN_3
4.22	3.59	15.13	NaOCN
4.78	3.39	16.20	$RbCrS_2$
5.27	3.03	15.96	$NaFeO_2$
5.47	3.71	20.29	$NaCrSe_2$
5.55	3.53	19.57	$NaCrS_2$
5.64	3.04	17.12	$CuFeO_2$
5.74	2.98	17.01	$CuCrO_2$
5.86	3.62	21.20	$KCrS_2$
7.03	3.44	24.20	$KCrSe_2$
7.84	3.43	26.90	$RbCrSe_2$
		$F5_{10}$	
2.38	7.39	17.58	$KAg(CN)_2$
		$F5_{12}$	
0.544	11.94	6.49	$Na_3(B_3O_6)$
0.573	12.79	7.33	$K_3(B_3O_6)$
		Ce_2O_2S	
1.71	4.01	6.83	Ce_2O_2S
1.71	4.04	6.89	La_2O_2S
1.73	3.93	6.77	Pu_2O_2S
		(See $D5_2$)	
		$PbSb_2O_6$	
0.913	5.27	4.81	$HgSb_2O_6$
0.915	5.24	4.80	$CdSb_2O_6$
0.943	4.78	4.50	$CoAs_2O_6$
0.960	5.23	5.02	$CaSb_2O_6$
0.985	5.26	5.34	$SrSb_2O_6$
1.01	4.83	4.87	$CdAs_2O_6$
1.01	5.30	5.37	$PbSb_2O_6$
1.03	4.84	4.98	$HgAs_2O_6$
1.05	4.83	5.08	$CaAs_2O_6$
1.08	5.30	5.75	$BaSb_2O_6$
1.11	4.85	5.41	$SrAs_2O_6$
1.13	4.87	5.49	$PbAs_2O_6$
		KUF_5	
0.664	14.71	9.77	$NaUF_5$
0.679	14.43	9.80	$NaPuF_5$
0.685	15.33	10.50	$KThF_5$
0.686	15.15	10.39	KUF_5
0.693	14.94	10.36	$KPuF_5$
0.696	15.22	10.61	$RbPuF_5$
		$G0_1$	
3.22	4.76	15.30	$ScBO_3$
3.23	4.64	14.98	$ZnCO_3$
3.24	4.60	14.91	$MgCO_3$
3.24	4.66	15.08	$CoCO_3$
3.24	4.78	15.49	$InBO_3$
3.25	4.68	15.23	$LiNO_3$
3.27	4.82	15.74	$MnCO_3$
3.27–3.29	4.91–4.95	16.07–16.28	(Cd, Mn)CO_3
3.28	4.68	15.36	$FeCO_3$
3.29	4.93	16.22	(Mn, Ca)CO_3
3.29	4.96	16.33	$CdCO_3$
3.32	5.06	16.81	$NaNO_3$
3.39	4.97	16.83	(Ca, Cd)CO_3
3.40	4.96	16.85	(Ca, Mn)CO_3
3.40	5.07	17.25	YBO_3
3.42	4.99	17.06	$CaCO_3$
		$G0_7$	
1.26	6.47	8.18	$CsBrO_3$[a]
1.30	6.20	8.09	NH_4BrO_3[a]
1.31	6.16	8.09	$TlBrO_3$[a]
1.31	6.20	8.12	$RbBrO_3$
1.34	6.06	8.15	$TlClO_3$
1.34	6.09	8.13	$RbClO_3$
1.36	6.02	8.16	$KBrO_3$
		$G1_1$	
3.28	4.86	15.95	$CaSn(BO_3)_2$
3.31	4.84	16.02	$CaMg(CO_3)_2$
3.34	4.83	16.15	Ca(Mg, Fe)$(CO_3)_2$
		$G2_2$	
0.576	11.75	6.77	$Nd(BrO_3)_3.9H_2O$
		$G3_2$	
1.13	5.45	6.14	Na_2SO_3
		$G7_1$	
1.37	7.10	9.74	(Ce, La, ...)FCO_3
5.24	4.36	22.80	$BaCO_3.2$(Ce, La, ...)FCO_3
6.82	4.10	27.99	$CaCO_3.2$(Ce, La, ...)FCO_3
		$RbNO_3$	
0.706	10.47	7.39	$RbNO_3$
0.715	10.76	7.70	$CsNO_3$
		$H1_3$	
0.660	12.63	8.33	Be_2GeO_4
0.661	14.29	9.45	$(Zn, Mn)_2SiO_4$
0.662	12.46	8.24	Be_2SiO_4
0.665	14.23	9.47	Li_2WO_4
0.665	14.24	9.47	Li_2MoO_4
0.667	14.22	9.48	Zn_2GeO_4
0.668	13.53	9.04	$LiAlSiO_4$
0.670	13.96	9.35	Zn_2SiO_4
0.673	13.19	8.87	Li_2BeF_4
		(See $S1_3$)	
		$H1_4$	
1.68	5.14	8.62	$KLiSO_4$
		(See $H2_8$)	
		$H2_8$	
1.68	5.17	8.67	$KAlSiO_4$
1.68	5.22	8.78	$BaAl_2O_4$
		(See $H1_4$)	
		$H3_2$	
1.69	4.72	7.98	$KAl(SO_4)_2$
1.70	4.75	8.05	$KCr(SO_4)_2$
1.72	4.84	8.33	$(NH_4)Fe(SO_4)_2$
1.74	4.73	8.25	$(NH_4)Al(SO_4)_2$
1.75	4.79	8.39	$(NH_4)Cr(SO_4)_2$
		$H4_{11}$	
0.332	15.97	5.30	$Cd(MnO_4)_2.6H_2O$[a]
0.334	15.49	5.18	$Ni(ClO_4)_2.6H_2O$
0.334	15.62	5.21	$Ni(MnO_4)_2.6H_2O$[a]
0.335	15.55	5.21	$Co(ClO_4)_2.6H_2O$
0.335	15.55	5.21	$Zn(ClO_4)_2.6H_2O$
0.336	15.61	5.25	$Fe(ClO_4)_2.6H_2O$
0.336	15.61	5.24	$Zn(MnO_4)_2.6H_2O$[a]
0.336	15.69	5.27	$Mg(MnO_4)_2.6H_2O$[a]
0.338	15.73	5.31	$Mn(ClO_4)_2.6H_2O$
0.339	15.55	5.27	$Mg(ClO_4)_2.6H_2O$
0.340	15.62	5.31	$Cd(ClO_4)_2.6H_2O$
		$H4_{18}$	
0.693	7.80	5.40	$LiMnO_4.3H_2O$
0.704	7.73	5.43	$LiClO_4.3H_2O$
		$H5_7$	
0.705	9.56	6.74	$Ca_{4.2}Mn_{0.6}Fe_{0.2}(OH)(PO_4)_3$
0.711	10.41	7.41	$Pb_5Cl(VO_4)_3$
0.712	9.57	6.81	$Ca_5Cl(PO_4)_3$
0.713	9.66	6.88	$Ca_9BaCl_2(PO_4)_6$
0.713	9.66	6.88	$Ca_9PbCl_2(PO_4)_6$
0.716	9.62	6.89	$Ca_9MgCl_2(PO_4)_6$
0.717	9.61	6.89	$Ca_9NiCl_2(PO_4)_6$
0.725	9.55	6.92	$Ca_{10}(F, OH)_2(SO_4.SiO_4)_3$
0.726	10.22	7.43	$Pb_5Cl(AsO_4)_3$
0.729	9.35	6.81	$(Ca, Mn)_5F(PO_4)_3$
0.729	9.43	6.87	$(Ca, Mg)_5OH(PO_4)_3$
0.729	9.45	6.89	$Ca_9PbO(PO_4)_6$
0.729	9.50	6.92	Wilkeite
0.729	9.62	7.01	$(Ca, Sr)_5(F, OH)[(P, As)O_4]_3$
0.730	9.43	6.89	$Ca_9NiO(PO_4)_6$
0.730	9.45	6.89	$Ca_9BaO(PO_4)_6$
0.730	9.45	6.89	$Ca_9SrO(PO_4)_6$
0.730	9.47	6.89	$Ca_9ZnCO_3(PO_4)_6$
0.731	9.42	6.89	$Ca_{10}CO_3(PO_4)_6.H_2O$
0.731	9.43	6.89	$Ca_9PbCO_3(PO_4)_6$
0.731	9.45	6.90	$Ca_9SrCO_3(PO_4)_6$
0.732	9.39	6.87	$Ca_5(Cl, F)(PO_4)_3$
0.732	9.45	6.91	$Ca_9BaCO_3(PO_4)_6$
0.733	9.44	6.92	$Ca_{10}O(PO_4)_6$
0.733	9.41	6.91	$Ca_5OH(PO_4)_3$
0.733	9.56	7.00	$Ca_{10}(OH)_2(SO_4.SiO_4)_3$
0.734	9.56	7.00	$Ca_{10}F_2(SiO_4.SO_4)_3$
0.735	9.37	6.89	Staffelite I
0.735	9.38	6.89	$Ca_9CdF_2(PO_4)_6$
0.735	9.38	6.89	$Ca_5F(PO_4)_3$
0.735	9.63	7.03	Britholite
0.736	9.14	6.72	$Ca_5Cd_5F_2(PO_4)_6$
0.736	9.35	6.88	Osteolite
0.736	9.62	7.08	$Ca_5Pb_5(OH)_2(PO_4)_6$
0.736	9.90	7.29	$Pb_5OH(PO_4)_3$
0.737	9.34	6.88	Podolite
0.737	9.35	6.89	Francolite
0.737	9.37	6.90	Lewistonite
0.737	9.53	7.02	$Ca_4Na_6F_2(SO_4)_6$
0.738	9.33	6.88	Staffelite II
0.738	9.33	6.88	Dehrnite
0.739	9.76	7.21	$Sr_5OH(PO_4)_3$
0.743	9.87	7.33	$Pb_5(Cl, F)(PO_4)_3$
0.744	9.27	6.89	$Ca_9(H_2O)_2(PO_4)_6$
0.750	9.29	6.96	$Ca_{10}CO_3H_2O(PO_4)_6$
0.751	10.22	7.68	$Ba_5OH(PO_4)_3$

[a] Original data.

[a] Original data.

Table IV. Hexagonal Substances Tabulated by Types (*Continued*)

c/a	a, A.	c, A.	Substance
		$CePO_4$	
0.908	6.99	6.35	$NdPO_4$
0.913	7.07	6.45	$CePO_4$
0.913	7.10	6.48	$LaPO_4$
0.928	6.97	6.47	$BiPO_4$
		Alunite	
2.27	7.19	16.33	$NaFe_3(SO_4)_2(OH)_6$
2.27	7.23	16.43	$AgFe_3(SO_4)_2(OH)_6$
2.34	7.21	16.83	$Pb_{0.5}Fe_3(SO_4)_2(OH)_6$
2.36	7.17	16.93	$(H_2O)Fe_3(SO_4)_2(OH)_5(H_2O)$
2.36	7.21	17.03	$KFe_3(SO_4)_2(OH)_6$
2.36	7.21	17.03	$NH_4Fe_3(SO_4)_2(OH)_6$
2.50	6.96	17.41	$KAl_3(SO_4)_2(OH)_6$
		$J1_2$	
1.96	6.53	12.78	$K_2Sn(OH)_6$
2.00	6.41	12.85	$K_2Pt(OH)_6$
2.38	5.96	14.20	$Na_2Sn(OH)_6$
		$J1_3$	
0.497	7.88	3.92	$CaCl_2.6H_2O$
0.498	7.99	3.98	$CaBr_2.6H_2O$
0.504	8.53	4.30	$SrI_2.6H_2O$
0.505	8.23	4.16	$SrBr_2.6H_2O$
0.506	8.40	4.26	$CaI_2.6H_2O$
0.515	7.93	4.08	$SrCl_2.6H_2O$
0.517	8.92	4.61	$BaI_2.6H_2O$
1.53	6.74	10.28	$K_2Pt(SCN)_6$
1.54	6.78	10.47	$(NH_4)_2Pt(SCN)_6$
1.55	6.76	10.49	$Rb_2Pt(SCN)_6$
		$J1_6$	
0.828	5.77	4.78	$(NH_4)_2SiF_6$ (See $J1_{13}$)
		$J1_{12}$	
1.91	5.24	10.00	$NaSbF_4(OH)_2$
		$J1_{13}$	
0.806	5.76	4.64	K_2PtF_6
0.812	7.44	6.04	Cs_2PuCl_6
0.814	5.71	4.65	K_2MnF_6
0.815	5.72	4.66	K_2TiF_6
0.816	5.86	4.79	$(NH_4)_2GeF_6$
0.823	5.83	4.80	Rb_2GeF_6
0.827	5.63	4.66	K_2GeF_6 (See $J1_6$)
		$J2_2$	
0.999	11.80	11.79	$Al(H_2O)_6Cl_3$
0.999	11.92	11.91	$Cr(H_2O)_6Cl_3$
		$J6_1$	
0.978	11.17	10.92	$Co(NH_3)_6Cr(CN)_6$
0.993	10.91	10.83	$Co(NH_3)_6Co(CN)_6$
1.01	9.64	9.70	$Fe(H_2O)_6SiF_6$
1.01	9.68	9.77	$Mn(H_2O)_6SiF_6$
1.01	9.79	9.87	$Mg(H_2O)_6TiF_6$
1.01	10.76	10.87	$Co(NH_3)_5H_2OCo(CN)_6$
1.01	10.77	10.86	$Co(NH_3)_5H_2OFe(CN)_6$
1.02	10.62	10.80	$Ni(H_2O)_6SnCl_6$
1.03	9.27	9.52	$Ni(H_2O)_6SiF_6$
1.03	9.33	9.65	$Zn(H_2O)_6SiF_6$
1.03	9.52	9.84	$Mg(H_2O)_6SiF_6$
1.03	9.57	9.90	$Zn(H_2O)_6TiF_6$
1.03	9.79	10.04	$Mg(H_2O)_6SnF_6$
1.03	9.79	10.13	$Zn(H_2O)_6ZrF_6$
1.03	10.62	10.91	$Co(H_2O)_6SnCl_6$[a]
1.03	10.70	10.97	$Fe(H_2O)_6SnCl_6$[a]
1.03	10.71	11.01	$Mg(H_2O)_6SnCl_6$[a]
1.04	9.33	9.72	$Co(H_2O)_6SiF_6$
1.04	10.66	11.06	$Mn(H_2O)_6SnCl_6$[a]
1.05	9.73	10.21	$Zn(H_2O)_6SnF_6$
1.06	(10.44)	(11.03)	$Co(NH_3)_4(H_2O)_2Co(CN)_6$
		$TlSbF_6$	
0.974	7.30	7.11	$BaGeF_6$
0.976	7.18	7.01	$BaSiF_6$
1.01	7.65	7.73	NH_4SbF_6
1.01	7.98	8.06	$CsSbF_6$
1.02	7.64	7.80	$RbSbF_6$
1.04	7.67	7.95	$TlSbF_6$
		$Mg(H_2O)_6SO_3$	
0.994	8.96	8.91	$MgSeO_3.6H_2O$
1.01	8.79	9.03	$NiSO_3.6H_2O$
1.03	8.84	9.06	$CoSO_3.6H_2O$
1.03	8.84	9.06	$MgSO_3.6H_2O$
		β_2-Na_2ThF_6	
0.612	6.13	3.75	$NaPuF_4$
0.614	6.15	3.78	$NaCeF_4$
0.618	6.54	4.04	K_2UF_6
0.619	6.18	3.83	$NaLaF_4$
0.629	5.95	3.74	Na_2UF_6
0.640	5.99	3.84	Na_2ThF_6

[a] Original data.

c/a	a, A.	c, A.	Substance
		β_1-K_2UF_6	
0.577	6.54	3.78	K_2UF_6
0.581	6.54	3.80	$KLaF_4$
0.581	6.58	3.82	K_2ThF_6
		$K1_1$	
0.635	10.13	6.43	$(NH_4)_2S_2O_6$[a]
0.637	10.05	6.39	$Rb_2S_2O_6$
0.643	9.80	6.30	$K_2S_2O_6$
0.650	9.09	5.91	$Na_2S_2O_6$[a]
		$K1_2$	
1.82	6.34	11.56	$Cs_2S_2O_6$
		$K7_1$	
2.26	7.17	16.19	$K_3W_2Cl_9$
2.26	7.17	16.19	$(NH_4)_3W_2Cl_9$
2.32	7.16	16.36	$Tl_3W_2Cl_9$
2.32	7.36	17.09	$Cs_3W_2Cl_9$
2.34	7.25	16.98	$Rb_3W_2Cl_9$
		$K7_2$	
1.43	12.84	18.32	$Cs_2Tl_2Cl_5$
		$K7_3$	
1.21	7.38	8.93	$Cs_3As_2Cl_9$
		OB4	
0.845	8.40	7.09	$NH(C_2H_5)_3Cl$
0.875	8.58	7.51	$NH(C_2H_5)_3Br$
0.882	8.80	7.76	$NH(C_2H_5)_3I$
		$OG1_1$	
1.16	7.28	8.46	$SbCl_2(CH_3)_3$
1.20	7.39	8.92	$SbBr_2(CH_3)_3$
1.27	7.55	9.61	$SbI_2(CH_3)_3$
		$OH6_2$	
3.08	7.15	22.06	$(NH_3CH_3)_2SnCl_6$
3.19	6.87	21.96	$(NH_3CH_3)_2PtCl_6$
		$OH6_7$	
1.16	7.25	8.43	$(NH_3C_2H_5)_2SnCl_6$
1.20	7.14	8.55	$(NH_3C_2H_5)_2PtCl_6$
		OI_1	
1.11	6.88	7.63	CHI_3
		OI_3	
0.929	9.29	8.63	$(CH_2O)_3$
		$O2_5$	
1.71	7.20	12.32	$C(NH_2)_3I$
		$O3_1$	
1.84	4.47	8.21	C_2H_6 (100° K.)
		$O5_7$	
0.329	16.40	5.40	$C_6(CH_2Br)_6$
		O7	
6.09	6.03	36.8	$C(CH_2O)_4(CHC_6H_5)_2$
		$O8_2$	
0.684	8.73	5.97	$C_3N_3(N_3)_3$
		$O8_5$	
0.641	10.25	6.57	$Na_2C_6N_9.3H_2O$
		$S1_3$	
0.661	14.29	9.45	$(Zn, Mn)_2SiO_4$
0.662	12.46	8.24	Be_2SiO_4
0.668	13.53	9.04	$LiAlSiO_4$
0.670	13.96	9.35	Zn_2SiO_4
		$S3_1$	
1.00	9.22	9.22	$Be_3Al_2(Si_6O_{18})$
		$S3_2$	
1.44	(6.73)	(9.72)	$BaTiGe_2O_9$
1.47	6.61	9.73	$BaTiSi_2O_9$
		$S3_3$	
0.406	12.70	5.17	$Ca_2Na_6[Al_2Si_2O_8]_3(CO_3)_2$
		$S3_4$	
1.09	13.78	14.98	$CaAl_2Si_4O_{12}.6H_2O$
		$S3_6$	
1.36	7.41	10.07	$Na_2ZrSi_3O_9.2H_2O$
		$S5_7$	
6.72	3.17	21.29	Cronstedtite

[a] Original data.

Table V. Hexagonal Substances Tabulated According to Axial Ratios

Table V lists 1278 hexagonal substances arranged in ascending order of their axial ratios. If two substances have the same value for c/a, the one with the smaller lattice constants is listed first. Column 4 also includes space group data where no definite structure has been established. To avoid repetition the various literature values (*2, 3, 5, 9–12, 14, 16–19*) have been averaged. All *kX* values have been converted to A.

c/a	a, A.	c, A.	Type	Substance
0.133	81.7	10.8	...	$C_{39}H_{76}O_5$, α,α'-distearin
0.147	64.7	9.5	...	$LiC_{18}H_{33}O_2$, Li oleate
0.157	62.6	9.8	...	$LiC_{18}H_{35}O_2$, Li stearate
0.181	52.7	9.5	...	$LiC_{14}H_{19}O_2$, Li undecylenate
0.182	24.45	4.45	R3*m*	$CHI_3.3S_8$
0.182	24.65	4.49	R3*m*	$AsI_3.3S_8$
0.183	60.1	11.0	...	$CH_3(CH_2)_{14}CO_2H$, palmitic acid
0.195	44.15	8.62	$P6_3$	$PbS.Sb_2S_3$, zinckenite
0.199	57.5	11.4	...	$CH_3(CH_2)_{12}CO_2H$, myristic acid
0.249	29.44	7.33	...	$TiBe_{12}$
0.255	22.11	5.63	$P\bar{3}$	*p*-$C_6H_4(OH)_2$, α-quinol
0.259	42.2	10.9	...	$LiC_8H_{15}O_2$, Li caprylate
0.284	21.5	6.10	$P3_1$	$C_{10}H_{19}OH$, *l*-menthol
(0.315)	(14.1)	4.45	...	$CHI_3.3S_8$
(0.316)	(14.2)	4.49	...	$AsI_3.3S_8$
0.317	27.06	8.57	...	$KAlSiO_4$, kaliophilite
0.323	9.86	3.19	B13	γ-NiSe
0.323	14.01	4.53	P31*c*	Cr_7C_3
0.324	20.50	6.64	R3*m*	$Pt[(NH_3)_5Cl]Cl_3.H_2O$
0.327	13.90	4.54	P31*c*	Mn_7C_3
0.327	16.66	5.44	$R\bar{3}$	$3C_6H_4(OH)_2.C_2H_2$
0.328–0.329	9.59–9.63	3.15–3.17	B13	NiS
0.329	16.40	5.40	$O5_7$	$C_6(CH_2Br)_6$
0.330	16.58	5.47	$R\bar{3}$	$3C_6H_4(OH)_2.HCl$
0.330	25.25	8.32	R3*m*	$[(C_3H_7)_2NCS_2]_2Ni$, Ni *N,N*-dipropyldithiocarbamate
0.331	16.60	5.49	$R\bar{3}$	$3C_6H_4(OH)_2.HBr$
0.331	16.61	5.50	$R\bar{3}$	$3C_6H_4(OH)_2.H_2S$
0.332	15.97	5.30	$H4_{11}$	$Cd(MnO_4)_2.6H_2O$
0.334	15.49	5.18	$H4_{11}$	$Ni(ClO_4)_2.6H_2O$
0.334	15.62	5.21	$H4_{11}$	$Ni(MnO_4)_2.6H_2O$
0.335	15.55	5.21	$H4_{11}$	$Co(ClO_4)_2.6H_2O$
0.335	15.55	5.21	$H4_{11}$	$Zn(ClO_4)_2.6H_2O$
0.335	16.59	5.56	R3	$3C_6H_4(OH)_2.CH_3OH$
0.336	15.61	5.25	$H4_{11}$	$Fe(ClO_4)_2.6H_2O$
0.336	15.61	5.24	$H4_{11}$	$Zn(MnO_4)_2.6H_2O$
0.336	15.69	5.27	$H4_{11}$	$Mg(MnO_4)_2.6H_2O$
0.337	9.06	3.06	$P6_3/m$	$3MgO(OH, F).BO_2$, fluoborite
0.338	15.73	5.31	$H4_{11}$	$Mn(ClO_4)_2.6H_2O$
0.339	15.55	5.27	$H4_{11}$	$Mg(ClO_4).6H_2O$
0.340	15.62	5.31	$H4_{11}$	$Cd(ClO_4)_2.6H_2O$
0.341	16.27	5.54	P3	*p*-$C_6H_4(OH)_2$, β-quinol
0.344	16.45	5.66	$R\bar{3}$	$3C_6H_4(OH)_2.HCOOH$
0.357	16.32	5.82	$R\bar{3}$	$3C_6H_4(OH)_2.SO_2$
0.360	11.06	3.99	$P6_3/m$	Th_7S_{12}
0.360	12.97	4.66	R3*m*	$CHI_3.3(C_9H_7N)$
.360	16.20	5.83	$R\bar{3}$	$3C_6H_4(OH)_2.CO_2$
0.365	27.8	10.1	...	$LiC_4H_7O_2$, Li butyrate
0.369	7.64	2.82	$P\bar{3}$	AgZn
0.369	7.80	2.88	...	γ-Ag_3Ga
0.377	11.58	4.36	$P6_3/m$	Th_7Se_{12}
0.382	10.46	3.99	R32, R3*m*	$Gd(OOCH)_3$
0.391	15.98	6.25	R3	$3C_6H_4(OH)_2.CH_3CN$
0.398	8.24	3.28	($P\bar{6}m2$)	$LiNaCO_3$
0.406	12.70	5.17	$S3_2$	$Ca_2Na_6[Al_2Si_2O_8]_3(CO_3)_2$
0.414	13.06	5.41	...	$KFeS_2$
0.416	74.89	31.12	R3	Insulin (dry)
0.418	12.83	5.36	$P6_3/mmc$	(Na, Ca)$_4$[AlSiO$_4$]$_3$(SO$_4$, CO$_3$, Cl), davynite
0.422	83.17	35.12	(R3)	Insulin (moist)
0.432	24.9	10.7	...	$LiC_4H_5O_2$, Li crotonate
0.435–0.454	15.75–16.01	6.86–7.24	R3*m*	(Na, Ca)(Mg, Fe)$_3$[B_3Al_6-Si_6O_{27}](O, OH, F)$_4$, tourmaline
0.436	28.41	12.39	...	$MnAl_4$
0.437	18.12	7.93	...	C_9Fe_{20}
0.472	16.14	7.62	...	Be(Ca, Mn)SiO_4, trimerite
0.479	21.8	10.46	...	Chitin
0.487	10.27	5.00	...	$C_{24}H_{36}$, perhydrocoronene
0.495	9.04	4.48	...	(Ni, Cu)$_3$P
0 497	7.88	3.92	($J1_3$)	$CaCl_2.6H_2O$
0 498	7.99	3.98	($J1_3$)	$CaBr_2.6H_2O$
0 504	8.53	4.30	($J1_3$)	$SrI_2.6H_2O$
0 505	8.23	4.16	($J1_3$)	$SrBr_2.6H_2O$
0.505	14.02	7.08	$P6_3/m$	$Nd(C_2H_5SO_4)_3.9H_2O$
0.505	14.11	7.12	$P6_3/m$	$La(C_2H_5SO_4).9H_2O$
0.506	8.4	4.26	($J1_3$)	$CaI_2.6H_2O$
0.506	13.94	7.05	$P6_3/m$	$Dy(C_2H_5SO_4)_3.9H_2O$
0.506	14.04	7.10	$P6_3/m$	$Pr(C_2H_5SO_4)_3.9H_2O$
0.506	14.08	7.12	$P6_3/m$	$Ce(C_2H_5SO_4).9H_2O$
0.507	13.93	7.06	$P6_3/m$	$Y(C_2H_5SO_4)_3.9H_2O$
0.507	13.96	7.07	$P6_3/m$	$Gd(C_2H_5SO_4)_3.9H_2O$
0.507	13.99	7.09	$P6_3/m$	$Sm(C_2H_5SO_4)_3.9H_2O$
0.511	6.77	3.46	C22	Pd_2Ge
0.515	7.93	4.08	($J1_3$)	$SrCl_2.6H_2O$
0.517	8.92	4.61	($J1_3$)	$BaI_2.6H_2O$
0.525	6.52	3.42	...	PdSi
0.526	6.75	3.55	C22	Pt_2Ge
0.527	13.32	7.01	R3	$BiCl_3.3CS(NH_2)_2$
0.528	6.48	3.42	...	(Pd_3B_2)
0.532	6.49	3.45	C22	Pd_2Si
0.534	14.69	7.85	$R\bar{3}$	CuH_2SiO_4, dioptase
0.536	13.47	7.21	$P\bar{3}m1$	(Mn, Fe)[Si_2O_7](Mn, Fe)$_3$-(OH, Cl)$_6$, pyrosmalite
0.544	11.94	6.49	$F5_{13}$	$Na_3(BO_2)_3$
0.545	10.67	5.82	...	$NaSrPO_4$
0.547	10.55	5.77	...	$NaCaPO_4$
0.549	10.72	5.88	...	$KSrPO_4$
0.551	10.62	5.85	...	$KCaPO_4$
0.551	10.97	6.04	$P\bar{3}m$	UCl_6
0.553	7.94	4.39	UCl_3	$PrBr_3$
0.554	7.93	4.39	UCl_3	α-$NpBr_3$
0.558	7.95	4.44	UCl_3	$CeBr_3$
0.559	7.94	4.44	UCl_3	UBr_3
0.563	6.27	3.53	UCl_3	$Dy(OH)_3$
0.565	6.25	3.53	UCl_3	$Er(OH)_3$
0.565	6.27	3.54	UCl_3	$Gd(OH)_3$
0.565	6.27	3.54	UCl_3	$Sm(OH)_3$
0.566	6.24	3.53	(UCl_3)	$Y(OH)_3$
0.566	7.97	4.51	UCl_3	$LaBr_3$
0.567	6.09	3.46	C22	Mn_2P
0.569	11.19	6.37	...	$Cu_{14}Al_5Mn$
0.573	7.40	4.24	UCl_3	$NdCl_3$
0.573	12.79	7.33	$F5_{13}$	$K_3(BO_2)_3$
0.574	7.40	4.25	UCl_3	$PuCl_3$
0.574	7.42	4.26	UCl_3	$PrCl_3$
0.575	4.37	2.52	...	γ'-$LiZn_3$
0.575	5.86	3.37	C22	Ni_2P
0.576	7.38	4.25	UCl_3	$AmCl_3$
0.576	11.75	6.77	$G2_2$	$Nd(BrO_3)_3.9H_2O$
0.577	6.51	3.76	$P\bar{6}2m$	β_1-$KCeF_4$
0.577	6.54	3.78	β_1-K_2UF_6	β_1-K_2UF_6
0.577	7.42	4.28	UCl_3	$NpCl_3$
0.577	15.82	9.14	...	$Cu_{19}Cl_4SO_4(OH)_{32}.3H_2O$ connellite
0.579	7.45	4.31	UCl_3	$CeCl_3$
0.580	8.08	4.69	UCl_3	$AcBr_3$
0.581	6.48	3.77	UCl_3	$Pr(OH)_3$
0.581	6.54	3.80	β_1-K_2UF_6	β_1-$KLaF_4$
0.581	6.58	3.82	β_1-K_2UF_6	β_1-K_2ThF_6
0.581	7.44	4.32	UCl_3	UCl_3
0.583	5.85	3.41	C22	(Ni, Cu)$_3$P
0.583	6.43	3.75	UCl_3	$Nd(OH)_3$
0.585	7.48	4.38	UCl_3	$LaCl_3$
0.589	5.87	3.46	C22	Fe_2P
0.590	6.54	3.86	UCl_3	$La(OH)_3$
0.592	20.3	12.04	...	$Na_2Ca(CO_3)$
0.594–0.598	5.68–5.65	3.38	...	Tl-Bi (20.5-57.1 at. % Tl)
0.596	11.91	7.07	...	Ni_3Sb
0.597	7.64	4.56	UCl_3	$AcCl_3$
0.598	5.50	3.29	$P6/mmm$	β-$BiIn_2$
0.601	20.2	12.17	...	Indigatin
0.609	16.05	9.79	$P\bar{3}1m$	$Ni(H_2O)_6[Sb(OH)_6]_2$
0.612	6.13	3.75	β_2-Na_2ThF_6	$NaPuF_4$
0.612	7.38	4.52	...	Al_8(Ta, Cb)$_4O_{19}$, simpsonite
0.612	16.11	9.86	$P\bar{3}1m$	$Mg(H_2O)_6[Sb(OH)_6]_2$
0.614	6.15	3.78	β_2-Na_2ThF_6	$NaCeF_4$
0.616	9.32	5.74	...	$4Na_2SO_4.CaSO_4$
0.618	6.54	4.04	β_2-Na_2ThF_6	β_2-K_2UF_6
0.619	6.18	3.83	β_2-Na_2ThF_6	$NaLaF_4$
0.623	12.72	7.93	$D8_{10}$	Cr_5Al_8
0.625	31.4	19.60	$R\bar{3}$	Tetramethylhematoporphyrin
0.629	5.95	3.74	β_2-Na_2ThF_6	β_2-Na_2UF_6
0.630	13.46	8.47	...	α-$Ag_{12}Te_7$
0.632	9.33	5.90	...	$(CH_3)_3N.BH_3$
0.635	10.13	6.43	$K1_1$	$(NH_4)_2S_2O_6$
0.637	10.05	6.39	$K1_1$	$Rb_2S_2O_6$
0.637	21.0	13.41	...	$K_2Ca(CO_3)_2$
0.640	5.99	3.84	β_2-Na_2ThF_6	β_2-Na_2ThF_6
0.641	10.25	6.57	$O8_5$	$Na_3C_6N_9.3H_2O$
0.643	9.80	6.30	$K1_1$	$K_2S_2O_6$
0.647	4.99	3.23	C32	UHg_2
0.649	13.47	8.74	...	$Mn_3As_2O_6$, armangite
0.650	9.09	5.91	$K1_1$	$Na_2S_2O_6$
0.651–0.654	7.91–7.85	5.14–5.13	...	$Ni_{10}Sb_{11}$
0.653	9.34	6.10	...	$(CH_3)_3N$-BF_3
0.658	19.04	12.53	...	$K_8BSiW_{12}O_{40}.18H_2O$
0.660	12.63	8.33	$H1_3$	Be_2GeO_4
0.661	14.29	9.45	$H1_3$, $S1_3$	(Zn, Mn)$_2SiO_4$, troostite
0.662	7.29	(4.83) × 2	...	$Ba(ClO_4)_2.3H_2O$
0.622	10.61	7.02	$P6_3/m$	$(CH_3)_2C{=}NOH$, acetoxime
0.662	12.46	8.24	$H1_3$, $S1_2$	Be_2SiO_4
0.664	14.71	9.77	KUF_5	$NaUF_5$
0.665	14.23	9.47	$H1_3$	Li_2WO_4
0.665	14.24	9.47	$H1_3$	Li_2MoO_4
0.667	14.22	9.48	$H1_3$	Zn_2GeO_4
0.668	13.53	9.04	$H1_3$, $S1_2$	α-$LiAlSiO_4$
0.668	13.60	9.09	($P6/mmc$)	$Cu_{19}SO_4Cl_4(OH)_{32}.3H_2O$, connellite
0.669	13.87	9.27	...	Ge_3N_4
0.670	13.96	9.35	$H1_3$, $S1_2$	Zn_2SiO_4
0.671	18.08	12.13	R3*m*	$COH(C_6H_5)_3$, triphenylmethanol
0.673	13.19	8.87	$H1_3$	Li_2BeF_4
0.675	13.55	9.15	($P6/mmc$)	$Cu_{19}(NO_3)_2Cl_4(OH)_{32}.3H_2O$, buttgenbachite
0.679	14.43	9.80	KUF_5	$NaPuF_5$
0.683	10.23	6.98	...	$Pb_2(AsO_3)_3Cl$, finnemanite
0.684	8.73	5.97	$O8_2$	$C_3N_3(N_3)_3$
0.685	15.33	10.50	KUF_5	$KThF_5$
0.686	15.15	10.39	KUF_5	KUF_5
0.693	7.80	5.40	$H4_{18}$	$LiMnO_4.3H_2O$
0.693	14.94	10.36	KUF_5	$KPuF_5$

Table V. Hexagonal Substances Tabulated According to Axial Ratios (*Continued*)

c/a	a, A.	c, A.	Type	Substance
0.696	6.91	4.81	$D8_9$	Mn_5Si_3
0.696	15.22	10.61	KUF_5	$RbPuF_5$
0.698	6.75	4.72	$D8_9$	Fe_5Si_3
0.704	7.73	5.43	$H4_{16}$	$LiClO_4.3H_2O$
0.705	9.56	6.74	$H5_7$	$Ca_{8.4}Mn_{1.1}Fe_{0.5}(PO_4)_6(OH)_2$
0.706	10.47	7.39	$RbNO_3$	$RbNO_3$
0.711	6.49	4.62	...	$ThAl_3$
0.711	10.41	7.41	$H5_7$	$Pb_5Cl(VO_4)_3$
0.712	9.57	6.81	$H5_7$	$Ca_5Cl(PO_4)_3$
0.713	9.66	6.88	$H5_7$	$Ca_9BaCl_2(PO_4)_6$
0.713	9.66	6.88	$H5_7$	$Ca_9PbCl_2(PO_4)_6$
0.715	10.76	7.70	$RbNO_3$	$CsNO_3$
0.716	9.62	6.89	$H5_7$	$Ca_9MgCl_2(PO_4)_6$
0.716	13.4	9.6	P3c1	Trinitrophloroglucinol
0.717	9.61	6.89	$H5_7$	$Ca_9NiCl_2(PO_4)_6$
0.718	8.26	5.93	$D8_8$	Mg_5Hg_3
0.725	9.51	6.88	...	$Na_2Ca_4(SO_4)_6F_2$
0.725	9.55	6.92	$H5_7$	$Ca_{10}(F, OH)_2(SiO_4.SO_4)_3$, ellestadite
0.726	10.22	7.43	$H5_7$	$Pb_5Cl(AsO_4)_3$, mimetite
0.729	9.35	6.81	$H5_7$	$(Ca, Mn)_5F(PO_4)_3$, manganapatite
0.729	9.43	6.87	$H5_7$	$(Ca, Mg)_5(OH)(PO_4)_3$
0.729	9.45	6.89	$H5_7$	$Ca_9PbO(PO_4)_6$
0.729	9.50	6.92	$H5_7$	Wilkeite
0.729	9.62	7.01	$H5_7$	$(Ca, Sr)_5(F, OH)[(P, As)O_4]_3$, fermorite
0.730	9.43	6.89	$H5_7$	$Ca_9NiO(PO_4)_6$
0.730	9.45	6.89	$H5_7$	$Ca_9BaO(PO_4)_6$
0.730	9.45	6.89	$H5_7$	$Ca_9SrO(PO_4)_6$
0.730	9.47	6.89	$H5_7$	$Ca_9ZnCO_3(PO_4)_6$
0.731	9.42	6.89	$H5_7$	$Ca_{10}CO_3(PO_4)_6.H_2O$, dahllite, quercyite
0.731	9.43	6.89	$H5_7$	$Ca_9PbCO_3(PO_4)_6$
0.731	9.45	6.90	$H5_7$	$Ca_9SrCO_3(PO_4)_6$
0.732	7.47	5.46	...	$LiI.3H_2O$
0.732	9.39	6.87	$H5_7$	$Ca_5(Cl, F)(PO_4)_3$
0.732	9.45	6.91	$H5_7$	$Ca_9BaCO_3(PO_4)_6$
0.733	9.44	6.92	$H5_7$	$Ca_{10}O(PO_4)_6$
0.733	9.56	7.00	$H5_7$	$Ca_{10}(OH)_2(SiO_4.SO_4)_3$
0.733	9.41	6.91	$H5_7$	$Ca_5OH(PO_4)_3$
0.734	9.0	6.62	...	$Cd_3(PO_4)_2$?
0.734	9.56	7.00	$H5_7$	$Ca_{10}F_2(SiO_4.SO_4)_3$
0.735	9.37	6.89	$H5_7$	Staffelite I
0.735	9.38	6.89	$H5_7$	$Ca_9CdF_2(PO_4)_6$
0.735	9.38	6.89	$H5_7$	$Ca_5F(PO_4)_3$
0.735	9.63	7.03	$H5_7$	(Ce, Ca, Na)$_5$(F, OH)[(Si, P)O_4]$_3$, britholite
0.736	9.14	6.72	$H5_7$	$Ca_5Cd_5F_2(PO_4)_6$
0.736	9.35	6.88	($H5_7$)	Osteolite
0.736	9.62	7.08	$H5_7$	$Ca_5Pb_5(OH)_2(PO_4)_6$
0.736	9.68	7.12	...	$Pb_3(PO_4)_2$?
0.736	9.90	7.29	$H5_7$	$Pb_{10}(OH)_2(PO_4)_6$
0.736	10.04	7.38	...	$Pb_3(AsO_4)_2$
0.737	9.34	6.88	$H5_7$	Podolite
0.737	9.35	6.89	$H5_7$	Francolite
0.737	9.37	6.90	$H5_7$	(Ca, K, Na, Al)$_5$OH$(PO_4)_3$, lewistonite
0.737	9.53	7.02	$H5_7$	$Ca_4Na_6F_2(SO_4)_6$
0.738	9.33	6.88	$H5_7$	Staffelite II
0.738	9.33	6.88	$H5_7$	(Ca, Na, K)$_5$OH$(PO_4,CO_3)_3$, dehrnite
0.739	9.76	7.21	$H5_7$	$Sr_5(OH)(PO_4)_3$
0.742	7.63	5.66	...	AgZn
0.743	9.87	7.33	$H5_7$	$Pb_5(Cl, F)(PO_4)_3$
0.744	9.27	6.89	$H5_7$	$Ca_9(H_2O)_2(PO_4)_6$
0.750	9.29	6.96	...	Bone
0.750	9.29	6.96	$H5_7$	$Ca_{10}CO_3H_2O(PO_4)_6$
0.751	10.22	7.68	$H5_7$	$Ba_5OH(PO_4)_3$
0.768	6.25	4.80	...	$LiHg_3$
0.779	5.43	4.23	Zn_5Ca	Zn_5La
0.781	5.40	4.22	Zn_5Ca	Zn_5Ca
0.787	12.7	10.0	...	$C_6H(OH)_2(NO_2)_3$, styphnic acid
0.790	11.09	8.76	R3c	Ag_3SbS_3, pyrargyrite
0.795	10.85	8.62	...	Cu_9Sb_2
0.796	4.96	3.95	Zn_5Ca	Ni_5Ca
0.796	5.17	4.12	Zn_5Ca	Cu_5La
0.796	5.33	4.25	$D0_{19}$	Ni_3In
0.796	(11.98)	(9.54)	...	B
0.798	5.66	4.52	...	$Mn_{11}Sn_2$
0.799	5.46	4.36	$D0_{19}$	Fe_3Sn
0.800	5.10	4.08	Zn_5Ca	Cu_5Ca
0.800–0.801	5.66–5.67	4.53–4.54	$D0_{19}$	β'-Mn-Sn (23-24.5 at. % Sn)
0.801	10.79	8.64	R3c	Ag_3AsS_3, proustite
0.802	5.29–5.31	4.24–4.26	$D0_{19}$	Ni_3Sn
0.803	4.95	3.97	Zn_5Ca	Ni_5Pr
0.804	5.14	4.13	Zn_5Ca	$Cu_{4.8}Ce_{1.2}$
0.805	5.13	4.13	$D0_{19}$	Co_3W
0.805	5.96	4.80	$D0_{19}$	$Ti_3(Sb_{0.8}Ti_{0.2})$
0.806	5.76	4.64	($J1_{18}$)	K_2PtF_6
0.807	5.28	4.26	B35	CoSn
0.808	4.96	4.01	Zn_5Ca	Ni_5La
0.809	6.28	5.08	$D0_{19}$	Mg_3Cd
(0.809)	(9.29)	(7.53)	$G0_1$	$CoCO_3$
0.810	6.23	5.05	$D0_{19}$	Cd_3Mg
0.811	4.91	3.98	Zn_5Ca	Ni_5Gd
0.811	4.92	3.99	Zn_5Ca	Ni_5Th
0.812	7.44	6.04	$J1_{13}$	Cs_2PuCl_6
0.813	10.91	8.87	...	$CaNd_2Si_2O_8$
0.813	10.91	8.87	...	$KNdSiO_4$
0.813	10.91	8.87	...	$NaNdSiO_4$
0.814	5.71	4.65	$J1_{13}$	K_2MnF_6
0.815	5.72	4.66	$J1_{13}$	K_2TiF_6
0.815	11.03	8.99	...	$KLaSiO_4$
0.816	4.95	4.04	Zn_5Ca	Co_5Th
0.816	5.86	4.79	$J1_{13}$	$(NH_4)_2GeF_6$
0.816	10.81	8.82	...	$CaY_2Si_2O_8$
0.816	10.81	8.82	...	$NaYSiO_4$
0.816	11.03	8.90	...	$CaLa_2Si_2O_8$
0.816	11.03	8.90	...	$NaLaSiO_4$
0.817	5.35	4.38	$D0_{19}$	$Mn_{3.25}Ge$
0.818	4.96	4.06	Zn_5Ca	Co_5Ce
0.822	4.87	4.00	Zn_5Ca	Ni_5Ce
0.823	5.83	4.80	$J1_{13}$	Rb_2GeF_6
0.827	5.63	4.66	$J1_{13}$	K_2GeF_6
0.828	5.61	4.65	B35	PtTl
0.828	5.77	4.78	$J1_6$	$(NH_4)_2SiF_6$
0.834	10.05	8.38	$P6_3$	$KNa_3[AlSiO_4]_4$, nepheline
0.836	14.3	11.95	...	δ_H-$C_6H_6Cl_6$
0.837	10.76	9.02	...	Ni_5Sb_{11}
0.839	5.30	4.45	B35	β-FeSn
0.845	8.40	7.09	OB4	$NH(C_2H_5)_3Cl$
0.846	5.24	4.45	Zn_5Ca	$Zn_{5.4}Th_{0.6}$
0.847	9.99	8.46	...	$NaAlSiO_4$, nephelite
(0.855)	(9.98)	(8.53)	$G0_1$	$CaCO_3$
0.857	9.27	7.95	...	$NaSrPO_4$
0.866	5.58	4.83	$P6_3mc$	$BaNiO_3$
0.875	8.58	7.51	OB4	$NH(C_2H_5)_3Br$
0.876	6.87	6.02	...	ICN
0.877	6.01	5.27	R3m	AgCN
0.882	8.80	7.76	OB4	$NH(C_2H_5)_3I$
0.884	7.87	6.95	...	Mg_2Ga
0.898	14.07	12.64	$R\bar{3}m$	$BiCo(CN)_6.6SC(NH_2)_2$
0.908	6.99	6.35	$P3_121$	$NdPO_4$
0.913	5.27	4.81	$PbSb_2O_6$	$HgSb_2O_6$
0.913	7.07	6.45	$P3_121$	$CePO_4$
0.913	7.10	6.48	$P3_121$	$LaPO_4$
0.915	5.24	4.80	$PbSb_2O_6$	$CdSb_2O_6$
0.919	5.36	4.93	...	$LiSb(OH)_6$
0.921	7.22	6.65	...	$AcPO_4.0.5H_2O$
0.923	6.77	6.25	...	$2(CaSO_4).\sim 1H_2O$
0.928	6.97	6.47	$P3_121$	$BiPO_4$
0.929	9.29	8.63	$O1_3$	$(CH_2O)_3$
0.930–0.931	3.21	2.98–2.99	...	Hg-Sn (21.95-3.8 at. % Hg)
0.932–0.933	4.81–4.76	4.48–4.44	...	$Cr_{2-x}N_{1+x}$ (27.6-33.4 at. % N)
0.935	3.77	3.52	P6/mmm	$Ni_{0.64}Li_{2.16}N$
0.940	3.19	3.00	...	$Sn_{12}Hg$
0.943	4.78	4.50	$PbSb_2O_6$	$CoAs_2O_6$
0.943	5.48	5.17	$E2_3$	$LiIO_3$
0.943	14.00	13.20	...	$(C_6H_5)_3CCl$
0.944	10.92	10.31	...	$CaCO_3.CaSO_4.CaSiO_3.-15H_2O$, thaumasite
0.945	6.21	5.87	$F0_2$	COS (<135° K.)
0.950	5.02	4.77	...	α-$Al(OH)_3$, bayerite
0.955	8.53	8.15	($P6_3/m$)	$AlBO_3$, jeremejevite
0.956	4.55	4.35	B35	ϵ-InNi
0.957	11.64	11.14	...	$(37Mn_5SiO_7.10Fe_3Sb_2O_8)$, langbanite
0.957	19.47	18.64	...	$(K, Na)_6Fe_3(SO_4)_6(OH)_2.-9H_2O$, metavoltine
0.960	5.23	5.02	$PbSb_2O_6$	$CaSb_2O_6$
0.960	12.02	11.54	...	CrS
0.961	3.74	3.62	P6/mmm	$Co_{0.68}Li_{2.32}N$
0.964	13.89	13.39	...	$(C_6H_5)_3CBr$
0.966	6.83	6.60	...	YPO$_4$
0.968	5.09	4.93	$R\bar{3}m$	Po (>348° K.)
0.969	2.90	2.81	...	MoC
0.974	7.30	7.11	$BaSiF_6$	$BaGeF_6$
0.976	2.91	2.84	...	WC
0.976	7.18	7.01	$BaSiF_6$	$BaSiF_6$
0.978	11.17	10.92	$J6_1$	$Co(NH_3)_6Cr(CN)_6$
0.980	2.87	2.81	...	MoN
0.980	10.22	10.02	...	$(Al_2O_3.4SiO_2.H_2O)$, fuller's earth
0.985	5.26	5.34	$PbSb_2O_6$	$SrSb_2O_6$
0.992	7.68	7.61	$D8_{11}$	Co_2Al_5
0.993	10.91	10.83	$J6_1$	$Co(NH_3)_6Co(CN)_6$
0.994	8.96	8.91	$Mg(H_2O)_6SO_3$	$MgSeO_3.6H_2O$
0.999	11.80	11.79	$J2_2$	$Al(H_2O)_6Cl_3$
0.999	11.92	11.91	$J2_2$	$Cr(H_2O)_6Cl_3$
1.00	4.28	4.28	C32	$PrGa_2$
1.00	4.31	4.31	C32	$CeGa_2$
1.00	4.32	4.32	C32	$CaGa_2$
1.00	9.22	9.22	$S3_1$	$Be_3Al_2(SiO_3)_6$, bery
1.01	4.83	4.87	$PbSb_2O_6$	$CdAs_2O_6$
1.01	5.30	5.37	$PbSb_2O_6$	$PbSb_2O_6$
1.01	7.65	7.73	$TlSbF_6$	NH_4SbF_6
1.01	7.98	8.06	$TlSbF_6$	$CsSbF_6$
1.01	8.79	9.03	$Mg(H_2O)_6SO_3$	$NiSO_3.6H_2O$
1.01	9.64	9.70	$J6_1$	$Fe(H_2O)_6SiF_6$
1.01	9.68	9.77	$J6_1$	$Mn(H_2O)_6SiF_6$
1.01	9.79	9.87	$J6_1$	$Mg(H_2O)_6TiF_6$
1.01	10.76	10.87	$J6_1$	$Co(NH_3)_5H_2OCo(CN)_6$
1.01	10.77	10.86	$J6_1$	$Co(NH_3)_5H_2OFe(CN)_6$
1.02	3.00	3.06	C32	VB_2
1.02	3.05	3.11	C32	MoB_2
1.02	3.68	3.77	...	$Cu_{0.40}Li_{2.60}N$
1.02	4.33	4.40	C32	$LaGa_2$
1.02	6.99	7.13	$D0_{21}$	Cu_3P
1.02	6.99	7.16	$D0_6$	SmF_3
1.02	7.07	7.23	$D0_6$	PrF_3

Table V. Hexagonal Substances Tabulated According to Axial Ratios (*Continued*)

c/a	a, A.	c, A.	Type	Substance
1.02–1.03	7.10–7.21	7.24–7.50	$P\bar{3}c1$	$Cu_{3+x}As_{1-x}$ (25.0-17.0 at. % As)
1.02	7.12	7.28	$D0_6$	CeF_3
1.02	7.13	7.29	$D0_6$	(Ce, La)F_3
1.02	7.14	7,29	$D0_6$	(La, Ce, Pr, . . .)F_3, tysonite, fluocerite
1.02	7.17	7.34	$D0_6$	LaF_3
1.02	7.64	7.80	$TlSbF_6$	$RbSbF_6$
1.02	10.62	10.80	$J6_1$	$Ni(H_2O)_6SnCl_6$
1.02	13.68	13.98	. . .	$Cu_2(OH)_3Cl$, paratacamite
1.03	4.84	4.98	$PbSb_2O_6$	$HgAs_2O_6$
1.03	7.03	7.21	$D0_6$	NdF_3
1.03	8.84	9.06	$Mg(H_2O)_6SO_3$	$CoSO_3.6H_2O$
1.03	8.84	9.06	$Mg(H_2O)_6SO_3$	$MgSO_3.6H_2O$
1.03	9.27	9.52	$J6_1$	$Ni(H_2O)_6SiF_6$
1.03	9.52	9.84	$J6_1$	$Mg(H_2O)_6SiF_6$
1.03	9.57	9.90	$J6_1$	$Zn(H_2O)_6TiF_6$
1.03	9.33	9.65	$J6_1$	$Zn(H_2O)_6SiF_6$
1.03	9.79	10.04	$J6_1$	$Mg(H_2O)_6SnF_6$
1.03	9.79	10.13	$J6_1$	$Zn(H_2O)_6ZrF_6$
1.03	10.62	10.91	$J6_1$	$Co(H_2O)_6SnCl_6$
1.03	10.70	10.97	$J6_1$	$Fe(H_2O)_6SnCl_6$
1.03	10.71	11.01	$J6_1$	$Mg(H_2O)_6SnCl_6$
1.04	6.32	6.56	. . .	$2Ca(OH)_2.Ca(OCl)_2$
1.04	7.12	7.44	. . .	PI_3
1.04	7.67	7.95	$TlSbF_6$	$TlSbF_6$
1.04	9.33	9.72	$J6_1$	$Co(H_2O)_6SiF_6$
1.04	10.66	11.06	$J6_1$	$Mn(H_2O)_6SnCl_6$
1.05	3.09	3.24	C32	TaB_2
1.05	3.86	4.07	C32	β-USi_2
1.05	3.97	4.17	$P3m1$	α-UO_3
1.05	4.83	5.08	$PbSb_2O_6$	$CaAs_2O_6$
1.05	6.63	6.93	$P\bar{6}2m$	$Al_3Si_6Mg_3Fe$
1.05	9.73	10.21	$J6_1$	$Zn(H_2O)_6SnF_6$
1.06	3.66	3.89	$P6/mmm$	Li_3N
1.06	10.44	11.03	$J6_1$	$Co(NH_3)_4(H_2O)_2Co(CN)_6$
1.06	22.4	23.7	$P3c1$	$(C_4H_9)_2P.CuI$
1.07	3.03	3.23	C32	TiB_2
1.07	3.09	3.31	C32	CbB_2
1.07	7.33	7.87	. . .	$Cu_{20}Sn_6$
1.08	3.01	3.25	C32	AlB_2
1.08	5.30	5.75	$PbSb_2O_6$	$BaSb_2O_6$
1.08	(5.73)	(6.19)	. . .	AlCu
1.08	6.14	6.60	$P6_3$	BCl_3 (~80° K.)
1.09	(3.60)	(3.92)	. . .	Cb_2O_5[a]
1.09	5.02	5.49	. . .	β-SiO_2, β-quartz (~870° K.)
1.09	13.78	14.98	$S3_4$	$CaAl_2Si_4O_{12}.6H_2O$, chabazite
1.10	4.01	4.41	. . .	Yttroparisite
1.10	4.73	5.19	(C8)	BeF_2
1.10	4.91	5.40	C8	α-SiO_2, α-quartz
1.10	6.19	6.79	. . .	W_2P
1.10	7.10	7.79	($BaSiF_6$)	β-KPF_6 (243° K.)
1.11	3.17	3.53	C32	ZrB_2
1.11	4.85	5.41	$PbSb_2O_6$	$SrAs_2O_6$
1.11	5.04	5.60	C8	$FePO_4$
1.11	6.88	7.63	$O1_1$	CHI_3
1.12	4.90	(5.47)	C8	$AlPO_4$
1.12	5.04	(5.62)	C8	$AlAsO_4$
1.13	4.53	5.51	$D5_{13}$	In_2Pt_3
1.13	4.87	5.49	$PbSb_2O_6$	$PbAs_2O_6$
1.13	4.99	5.65	C8	GeO_2
1.13	5.45	6.14	$G3_2$	Na_2SO_3
1.13	8.59	9.7	. . .	$Al_3Mn_{13}O_{28}.8H_2O$
1.14	4.35	4.96	A8	Se
1.16	3.56	4.12	. . .	Ca_3N_2
1.16	6.22	7.2	. . .	$ZnF_2.4Zn(OH)_2$
1.16	7.25	8.43	$OH6_7$	$(NH_3C_2H_5)_2SnCl_6$
1.16	7.28	8.46	$OG1_1$	$SbCl_2(CH_3)_3$
1.17	8.41	9.8	. . .	$Mn_{16}O_{28}.8H_2O$
1.17	8.41	9.8	. . .	$Zn_2Mn_{14}O_{28}.8H_2O$
1.17	9.74	11.33	. . .	$MnCl_2.2MgCl_2.12H_2O$
1.17–1.19	11.81–12.08	13.77–14.42	R3c	$K_3NaFeCl_6$, rinneite
1.18	4.40	5.25	$D5_{12}$	δ'-InNi
1.18	9.44	11.09	. . .	$CdCl_2.2NiCl_2.12H_2O$
1.18	11.49	13.58	R3c	CH_3CONH_2
1.20	6.15	7.37	. . .	δ-Na_2ThF_6
1.20	7.14	8.55	$OH6_7$	$(NH_3C_2H_5)_2PtCl_6$
1.20	7.39	8.92	$OG1_1$	$SbBr_2(CH_3)_3$
1.20	8.41	10.1	. . .	$Na_2Mn_{14}O_{28}.8H_2O$
1.20	10.80	12.91	. . .	CuPt
1.21	4.04	4.90	$D5_{13}$	Ni_2Al_3
1.21	4.06	4.90	$D5_{13}$	Ga_3Ni_2
1.21	4.20	5.10	B8	CuSn
1.21	4.53	5.50	$D5_{12}$	In_2Pd_3
1.21	5.41	6.57	$P6/mmc$	$(NO_2^+)(NO_3^-)$ (213° K.)
1.21	5.72	6.9	. . .	$2Ca(OH)_2.Al(OH)_2Cl$
1.21	5.73	6.95	. . .	$BaTiO_3$
1.21	7.38	8.93	$K7_3$	$Cs_2As_2Cl_9$
1.22	5.45	6.66	$P6/mmc$	$(NO_2^+)(NO_3^-)$ (293° K.)
1.22	11.15	13.66	. . .	$Ni_3Pb_2S_2$, shandite
1.23	4.18–4.19	5.13–5.16	B8	$NiIn_{1-x}$
1.23	4.23	5.18	$D5_{13}$	Ga_3Pt_2
1.23	4.23	5.21	B8	γ-FeSn (~44 at. % Sn)
1.23	4.28	5.25	B8	$CuIn_{1-x}$
1.23	5.74	7.03	R32	Ni_3S_2
1.23	6.31	7.79	. . .	$4Zn(OH)_2.ZnCl_{2-x}(OH)_x$; x = 0.70 to 0.75
1.23–1.25	8.63–8.75	10.67–10.80	. . .	SnSb (45-55 at. % Sb)
1.24–1.25	4.40–4.38	5.47–5.49	B8	$MnSn_{1-x}$ (28.6-36.1 at. % Sn)
1.24	4.51	5.57	. . .	Ice(II) (118° K.)
1.24	(4.65)	(5.76)	. . .	Co_2O_3
1.24	5.73	7.1	. . .	$2Ca(OH)_2Al(OH)_2Br$
1.24	6.15	7.61	. . .	$CaCO_3.H_2O$
1.24	11.93	14.78	$R\bar{3}c$	K_4MnCl_6, chloromanganokalite
1.25	4.04	5.03	B8	$FeGe_{1-x}$
1.25	6.23	7.81	$R\bar{3}$	$TlIO_3$
1.26	4.05–4.15	5.12–5.21	B8	$CoSn_{1-x}$ (39.4-42.2 at. % Sn)
1.26–1.27	4.15–4.05	5.21–5.12	B8	$NiSn_{1-x}$ (39-42 at. % Sn)
1.26	4.09	5.15	B8	FeSb
(1.26)	4.09	(5.15)	. . .	Sn_3As_2
1.26	11.86	14.9	$R\bar{3}c$	K_4CdCl_6
1.26	12.48	15.71	($R\bar{3}m$)	$(NH_4)_4CdCl_6$
1.26	12.59	15.87	. . .	$ZnCl_2.4Zn(OH)_2$
1.265	6.47	8.18	$G0_7$	$CsBrO_3$
1.27	4.04	5.13	C6	$PdTe_2$
(1.27)	4.93	(6.25)	. . .	AlF_3
(1.27)	5.23	(6.65)	. . .	FeF_3
1.27	7.55	9.61	$OG1_1$	$SbI_2(CH_3)_3$
1.28–1.30	3.96–3.85	5.05–4.99	B8	$NiGe_{1-x}$
1.28	3.93	5.01	B8	$CoGe_{1-x}$
1.28	4.25	5.46	B8	PtPb
1.28	4.34	5.56	B8	$RhSn_{1-x}$
1.28	4.35	5.55	B8	AuSn
1.28	4.46–4.49	5.69–5.74	B8	$PdPb_{1-x}$
1.29	3.96	5.12	. . .	Ir_3Si_2
1.29	4.40–4.38	5.66–5.63	B8	$PdSn_{1-x}$ (36-42 at. % Sn)
1.29	5.64	7.28	$P\bar{3}m1$	$KNaSO_4$, aphthitalite
1.29	5.91	7.63	$P6/mmc$	$C_{18}H_{24}$, dodecahydrotriphenylene
1.30	4.02	5.21	C6	$PtTe_2$
1.30	5.65	7.36	$P\bar{3}m1$	$BaNaPO_4$
1.30	5.67	7.34	$P\bar{3}m1$	$NaK_3(SO_4)_2$, glaserite
1.30	6.20	8.09	$G0_7$	NH_4BrO_3[a]
1.30	7.61	9.87	$P31c$	$NaLiSO_4$
1.30	10.29	13.35	R3c	P_4O_{10}
1.31	3.92	5.14	B8	Ni(Sb, As) (10 mole % AsNi)
1.31	3.94	5.15	B8	NiSb, breithauptite
1.31	5.39	7.06	$P\bar{3}m1$	$2Ca_2SiO_4.Ca_3(PO_4)_2$
1.31	6.16	8.09	$G0_7$	$TlBrO_3$
1.31	6.20	8.12	$G0_7$	$RbBrO_3$
(1.31)	(8.62)	11.24	A7	Sb
(1.31)	(8.63–9.04)	11.27–11.81	A7	Sb-Bi (16-94 at. % Bi)
(1.31)	(8.64)	11.31	A7	Pb_3Sb_7
(1.31)	(9.07)	11.85	A7	Bi
1.32	4.08	5.36	B8	NiBi
1.32	4.11	5.44	B8	PtSn
1.32	4.14	5.46	B8	PtTe
1.32	5.22	6.91	$P3m1$	$Ca_2SiO_4.Ca_3(PO_4)_2$
1.32	5.76	7.61	. . .	O_2 (48° K.)
1.32	7.29	9.66	. . .	$Ba(ClO_4)_2.3H_2O$
1.32–1.34	8.58–8.54	11.34–11.43	A7	Sn-Sb (2-20 at. % Sn)
1.33	4.12	5.48	B8	CrSb
1.33	4.14	5.48	B8	PtSb
1.33	4.46	5.92	A8	Te
(1.33–1.39)	(5.4)	(7.2–7.5)	. . .	$Al_2[Si_2O_5](OH)_4(^2/_3$-$^1/_3)H_2O$, (metahalloysite)
1.33	5.73	7.6	. . .	$2Ca(OH)_2.Al(OH)_2I$
1.33	8.24	(11.0)	$P6_122$	$[CH_3(CH_2)_{n-2}CH_3]_r.(NH_2)_2CO$
1.33	10.45	13.89	$P6/mcc$	$KCa_2(Be, Al)_2[Si_2O_8]_6$. milarite
1.34	3.48	4.67	C6	$Cd(OH)_2$
1.34	3.88	5.19	B8	CoSb
(1.34)	(4.89)	(6.55)	. . .	MoC
1.34	5.49	7.37	$P\bar{3}m1$	$SrNaPO_4$
1.34	6.06	8.15	$G0_7$	$TlClO_3$
1.34	6.09	8.13	$G0_7$	$RbClO_3$
1.35	5.39	7.27	$P\bar{3}m1$	Na_2SO_4
1.35	5.63	7.59	. . .	$K_2O.2PbO.2SiO_2$
1.35	11.51	15.55	$P\bar{3}c1$	$Cr(NH_2.CH_2.CH_2.NH_2)_3Cl_3.3H_2O$
1.35	11.88	15.50	$P\bar{3}c1$	$Co(NH_2.CH_2.CH_2.NH_2)_3Cl_3.3H_2O$
1.36	3.08	4.19	. . .	PtO_2
1.36	3.73	5.07	C6	$PtSe_2$
1.36	3.76	5.10	B8	NiAs.NiSb
1.36	3.96	5.37	B8	NiTe
1.36	5.24	7.14	$P\bar{3}m1$	$CaNaPO_4$
1.36	5.59	7.62	$P\bar{3}m1$	$CaKPO_4$
1.36	5.74	7.8	. . .	$2Ca(OH)_2.Al(OH)_2Cl.2H_2O$
1.36	6.02	8.16	$G0_7$	$KBrO_3$
1.36	7.41	10.07	$S3_6$	$Na_2ZrSi_3O_9.2H_2O$, catapleite
1.36	11.52	15.67	$P\bar{3}c1$	$Rh(NH_2.CH_2.CH_2.NH_2)_3Cl_3.3H_2O$
1.37	3.41	4.67	C6	$Cd(OH)_2$-$Mn(OH)_2$
1.37	3.86	5.28	C6	$NiTe_2$
1.37	4.08	5.59	B8	PdSb
1.37	4.14	5.67	B8	PdTe
1.37	6.26	8.61	$F5_1$	$AgFeO_2$
1.37	7.10	9.74	$G7_1$	(Ce, La, . . .)FCO_3, bastnasite
1.37	11.88	16.32	$P\bar{3}c1$	$Cr(NH_2.CH_2.CH_2.NH_2)_3Br_3.3H_2O$
1.38	3.25	4.48	C6	$Fe(OH)_2$

[a] Original data.

Table V. Hexagonal Substances Tabulated According to Axial Ratios (*Continued*)

c/a	a, A.	c, A.	Type	Substance
1.38	3.50–3.52	4.83–4.85	C6	$Ca(OH)_2$-$Cd(OH)_2$ [25-75 mole % $Ca(OH)_2$]
1.38	3.59	4.94	C6	$Ca(OH)_2$
1.38–1.43	3.89–3.79	5.38–5.41	C6	$CoTe_{2-x}$ (50.0-66.7 at. % Te)
1.38	3.90	5.37	B8	CoTe
1.38	5.72	7.88	$P\bar{3}m1$	K_2SO_4
1.38	11.63	16.04	$P\bar{3}c1$	$Co(NH_2.CH_2.CH_2.NH_2)_3$-$Br_3.3H_2O$
1.39	3.61	5.02	B8	(AsNi-SbNi), niccolite
1.39	3.63	5.05	B8	AsNi-SbNi (90 mole % AsNi)
(1.39)	4.14	(5.71)	...	Bi Se_3
(1.39)	4.35	(6.05)	...	Bi_2Te_3
1.40	3.59	5.01	C6	$CdCl_2.4Cd(OH)_2$
1.40	3.62	5.05	B8	NiAs
1.40	3.99	5.57	B8	IrSn
1.40	4.13	5.79	B8	MnSb
1.41	3.32	4.69	C6	$Mn(OH)_2$, pyrochroite
1.41	5.75	8.1	...	$2Ca(OH)_2.Al(OH)_2Br.2H_2O$
1.41	11.20	15.79	$R\bar{3}m$	$CH_3CH(OH)NH_2$
1.42	3.55	5.03	C6	PtS_2
1.42	3.77	5.33	...	CrAs
1.42	4.31	6.13	B8	MnBi
1.43	3.54	5.04	...	$CdCl_{0.26}(OH)_{1.74}$
1.43	3.79	5.41	C6	$CoTe_2$
(1.43)	4.25	(6.07)	...	Sb_2Te_3
1.43	12.84	18.32	$K7_2$	$Cs_3Tl_2Cl_9$
1.44	4.43	6.36	C40	$CrSi_2$
1.44	6.73	9.72	$(S3_2)$	$BaTiGe_3O_9$
1.44	10.57	15.19	...	(Na, Ca, Ce, Th)$_2$(Mn, Fe, Sb)[(Si, P)$_2$(O, OH, F)$_{12}$], steenstrupine
1.46	3.19	4.65	C6	$(Co, Zn)(OH)_2$
1.46	3.19	4.66	C6	$Zn(OH)_2$
1.46	3.20	4.66	C6	$Co(OH)_2$
1.46	3.62	5.29	B8	CoSe
1.46	3.67	5.34	B8	NiSe
1.46	7.43	10.59	...	Mg_2C_3
1.47–1.49	3.17–3.12	4.66–4.64	C6	$Co(OH)_2$-$Ni(OH)_2$ [30-80 mole % $Co(OH)_2$]
1.47	3.14	4.62	C6	$(Ni, Zn)(OH)_2$
1.47	3.33	4.89	...	UHg_3
1.47	3.39	4.99	...	CdF_2.(2-9)$Cd(OH)_2$
1.47	6.61	9.73	$S3_2$	$BaTiSi_3O_9$, benitoite
1.48	3.11	4.61	C6	$Ni(OH)_2$
1.48	3.16	4.67	C6	$Co(OH)_2$-$Mg(OH)_2$
1.48	3.16	4.67	C6	$Co(OH)_2$-$Zn(OH)_2$ [25 m e % $Zn(OH)_2$]
1.49	3.81	5.66	B8	FeTe
1.49	12.22	18.21	R3	Tl_2S
1.50	3.41	5.10	...	AuCN
1.50	5.74	8.6	...	$2Ca(OH)_2.Al(OH)_2NO_3$ $2H_2O$
1.51	3.10	4.68	C6	$Ni(OH)_2$-$Mg(OH)_2$
1.51	4.55	6.89	C6	PbI_2(I)
1.51	12.41	18.72	...	$Ca(H_2O)_4S_2O_6$
1.51	14.13	21.34	R3m	$(C_6H_5)_3CBr$
1.52	3.05	4.67	C6	$Ni(OH)_2$-$Zn(OH)_2$ [35 mole % $Zn(OH)_2$]
1.52	3.13	4.74	C6	$Mg(OH)_2$
1.52	7.1	10.8	...	β-Be (900° K.)
1.52	14.93	22.6	...	$2,4,6\text{-}C_6H_2Br(NO_2)_2$
1.53	3.39	5.19	B8	CoS
1.53	3.72	5.71	B8	MnAs
1.53	4.23	6.47	...	BiTeBr
1.53	5.75	8.8	...	$2Ca(OH)_2.Al(OH)_2I.$-$1.3H_2O$
1.53	6.74	10.28	$J1_3$	$K_2Pt(SCN)_6$
1.54	3.10	4.77	...	$Zn(OH)_2$-$Mg(OH)_2$ [25 mole % $Zn(OH)_2$]
1.54	4.25	6.54	C6	ZnI_2
1.54	6.78	10.47	$J1_3$	$(NH_4)_2Pt(SCN)_6$
1.54	12.48	19.28	...	$Sr(H_2O)_4S_2O_6$
1.55–1.56	2.76–2.77	4.30	A3	$Cu_{1-x}Zn_{3+x}$ (79.8-85.6 at. % Zn)
1.55–1.56	3.42–3.43	5.32–5.34	B8	β-NiS
1.55	3.59	5.55	C6	$CdCl_{0.56-0.67}(OH)_{1.44-1.33}$
1.55	4.08	6.30	$D5_2$	Ac_2O_3
1.55	4.49	6.97	C6	CaI_2
1.55	4.49	6.97	C6	YbI_2
1.55	5.75	8.9	...	$2Ca(OH)_2.Al(OH)_2.{}^1/_2SO_4.$-$nH_2O$
1.55	6.76	10.49	$J1_3$	$Rb_2Pt(SCN)_6$
1.56	2.82	4.39–4.38	...	$AuZn_7$ (86.3-88.8 at. % Zn)
1.56–1.58	2.83	4.47–4.39	...	$AgZn_3$ (86-70 at. % Zn)
1.56	(3.08)	(4.82)	...	LiMg (78° K.)
1.56	3.85	6.02	$D5_2$	Nd_2O_3
1.56	3.86	6.01	$D5_2$	Pr_2O_3
1.56	3.89	6.07	$D5_2$	Ce_2O_3
1.56	3.94	6.13	$D5_2$	La_2O_3
1.56	3.98	6.21	B8	CrTe
1.57	2.29	3.59	...	α-Au-Be
1.57	2.76	4.33	...	Cu_3Sn (54-66 wt. % Cu)
1.57	2.79	4.40	...	β′-Li-Zn (10.5 at. % Li)
1.57	3.37	5.30	B8	(Fe, Co)S
1.57	5.75	9.5	...	$2Ca(OH)_2.Al(OH)_2ClO_4$
1.57	11.40	17.91	...	$\beta\text{-}Al_{3+x}Mg_{2-x}$ (65 at. % Al)
1.58	2.29	3.61	A3	α-Be
1.58–1.62	2.72–2.63	4.29–4.25	...	Os-Ir [44.3-64.3% (Os + Ru)]
1.58–1.59	2.78–2.73	4.38–4.33	...	Cu_3Sb (25-19 at. % Sb)
1.58	2.75	4.34	...	Fe_2C
1.58–1.59	2.86–2.87	4.53–4.55	...	$V_{2+x}C_{1-x}$ (11.8-31.5 at. % C)
1.58–1.62	2.90–2.88	4.58–4.66	...	$\gamma\text{-}Ag_{3-x}Al_{1+x}$ (43-27 at. % Al)
1.58	3.00	4.72	...	W_2C
1.58	3.01	4.74	...	Mo_2C
1.58	3.05–3.10	4.82–4.90	...	$AgCd_3$ (69-83 at. % Cd)
1.58	3.52	5.57	A3	Lu
1.58	3.54	5.60	A3	Er
1.58	3.56	5.63	A3	Ho
1.58	3.59	5.66	A3	Dy
1.58	3.60	5.67	A3	Tb
1.58	4.31	6.83	...	BiTeI
1.58	4.58	7.24	$D5_2$	Mg_3Sb_2
1.58	5.51	8.71	...	$Cu_{11}Sb_4$
1.58–1.61	5.64–5.54	8.92–8.90	...	ε-Mn-Zn (11.58-14.3 at. % Mn)
1.59	2.70	4.28	A3	Ru
1.59	2.72	4.32	A3	Os
1.59	2.73	4.34	...	Cu_2SnFe
1.59–1.63	2.89–2.87	4.58–4.66	...	$Ag_{5+x}Al_{3+x}$ (43-27 at. % Al)
1.59	3.09	4.90	...	$LiCd_3$
1.59	3.21	5.09	A3	Hf
1.59	3.23	5.15	A3	α-Zr
1.59	3.31	5.25	A3	Sc
1.59	3.53	5.57	A3	Tm
1.59	3.63	5.76	A3	Gd
1.59	3.65	5.81	A3	Y
1.59	3.69	5.86	C6	ZrS_2
1.59	3.88	6.19	$D5_2$	Th_2N_3
1.59	4.68	7.42	$D5_2$	Mg_3Bi_2
1.60	2.54–2.55	4.07–4.09	...	Mn-Fe (13.4-32.4 at. % Mn)
1.60–1.61	2.61–2.67	4.16–4.31	...	Ni-N
1.60	2.64	4.21	...	Cu_3Ge
1.60–1.62	2.78–2.70	4.44–4.37	...	$Fe_{2+x}N_{1-x}$ (33.1-24.5 at. % N)
1.60	2.73	4.34	...	Os-Ru
1.60	2.74	4.39	A3	Tc
1.60–1.61	2.75–2.76	4.39–4.43	...	ε-CFeN
1.60	2.76	4.41	...	$MnZn_7$
1.60–1.63	2.84–2.78	4.54–4.53	...	Mn_3N (35.0-27.2 at. % N)
1.60	2.84	4.54–4.55	...	V_2N (42-27 at. % N)
1.60	2.90	4.62	B4	CuH
1.60	2.95	4.71	A3	Ti
1.60–1.61	2.97–3.00	4.76–4.84	...	Ag-Hg (37.0-44.8 at. % Hg)
1.60	3.10	4.94	C6	Ta_2C
1.60	3.12	4.99	B4	AlN
1.60	3.26	5.21	B4	ZnO
1.60	3.28	5.26	B4	ZnO-MnO (22 mole % MnO)
1.60	3.42	5.47	B8	(Ni, Fe)S
1.60	3.45	5.52	A3	Tl
1.60	3.46	5.53	...	$NaTl_3$
1.60–1.63	3.61–3.69	5.78–6.03	...	Cr-Se (60-53.5 at. % Se)
1.60	3.26	5.23	B4	ZnO-CdO (5 mole % CdO)
1.60–1.64	4.53–4.38	7.24–7.16	...	$(Mg, Zn)_3Sb_2$ (12.3-64.7 at. % Zn)
1.60	4.40	7.03	B4	NH_4F
1.60	4.90	7.85	...	$\gamma\text{-}Mg_3Ag$ (20-25 at. % Ag)
1.60	4.96	7.94	...	BiSe
1.60	5.74	9.2	...	$2Ca(OH)_2.Al(OH)_2ClO_3$
1.61	2.54–2.53	4.09–4.08	...	Mn-Fe (87.4-77.5 at. % Fe)
1.61–1.62	2.71	4.37–4.38	...	Fe_3N (24.9-27.3 at. % N)
1.61–1.63	2.76–2.73	4.44–4.45	...	Mn-Zn (16-50 at. % Mn)
(1.61)	(2.76–2.78)	4.44–4.48	P321	$Cr_{2+x}N_{1-x}$ (33.4-27.6 at. % N)
1.61	2.76	4.46	A3	Re
1.61	2.80	4.49	(A3)	$Fe_{1-x}Zn_{7+x}$ (87-92 at. % Zn)
1.61–1.63	2.98–2.95	4.79	...	$Ag_{3-x}In_{1+x}$, x = 0 to 1
1.61	2.97	4.78	...	$TiN_{0.22}$
1.61	2.99	4.81	...	Ag_3Sn
1.61	2.99	4.82	...	Ag_3Sb
1.61	3.10	4.99	...	(Al_2O)
1.61	3.54	5.70	B4	InN
1.61	3.65	5.88	C6	SnS_2
1.61	3.67	5.89	A3	Nd
1.61	3.80	6.12	B8	VTe
1.61	4.26	6.86	C6	CdI_2
1.61	6.64	10.66	C14	$BaMg_2$
1.61	10.68	17.19	B30	MgZn
1.62	2.51	4.07	A3	β-Co
1.62	2.55	4.12	...	$MnFe_5$ (77-88 at. % Fe)
1.62	2.61	4.22	...	$Cu_{3-x}As_{1+x}$
1.62	2.66	4.31	...	(Ni)
1.62	2.71–2.73	4.38–4.41	...	Fe_4N
1.62	2.93	4.75	...	$\beta\text{-}Ag_3Ga$ (>713° K.)
1.62–1.65	2.94–2.90	4.77–4.79	...	Au-Sn (20.8-8.0 at. % Sn)

Table V. Hexagonal Substances Tabulated According to Axial Ratios (*Continued*)

c/a	a, A.	c, A.	Type	Substance
1.62–1.65	2.94–2.91	4.76–4.80	...	β-$Au_{5+x}Sn_{1-x}$ (16-12 at. % Sn)
1.62–1.63	2.97–2.93	4.80–4.79	...	Ag-Sb (16-10 at. % Sb)
1.62–1.63	2.96–2.94	4.77–4.78	...	Ag_5Sn (19.7-13.3 at. % Sn)
1.62	3.00	4.86	...	AgHg
1.62	3.02	4.89	...	AgCd
1.62	3.06	4.95	B4	TaN
1.62–1.63	3.19–3.10	5.16–5.04	A3	Mg-Cd (80-42 at. % Mg)
1.62	3.20	5.18	A3	δ-(Mg, Ag) (3 at. % Ag)
1.62–1.63	3.20–3.21	5.19–5.21	A3	Mg-Zn (3-0 at. % Zn)
1.62–1.63	3.60–3.69	5.82–6.03	B8	$(Cr_{1-x}Se)$
1.62	3.66	5.91	A3	Pr
1.62	3.66	5.94	A3	β-Ce
1.62	3.75	6.07	A3	α-La
1.62	3.83	6.20	C6	$MnBr_2$
1.62	3.98	6.44	B4	MnS
1.62	4.13	6.71	B8	MnTe
1.62	4.14	6.71	B4	CdS
1.62	4.17	6.76	...	C_x
1.62	4.22	6.84	C14	$FeBe_2$
1.62	4.54	7.36	B4	MgTe
1.62	5.71	9.27	...	K_2GeF_6
1.62	5.86	9.50	...	Rb_2MnF_6
1.62	5.94	9.63	...	Rb_2GeF_6
1.62	6.23	10.12	C14	$CaMg_2$
1.63	2.56–2.69	4.17–4.39	...	Ni-H
1.63	2.60	4.19	...	Cu_6Si
1.63	2.60	4.23	...	Cu_2As
1.63	2.60	4.24	...	β-Cu_5Si (14.5 at. % Si)
1.63	2.70	4.38	B4	BeO
1.63	2.73	4.43	A3	β-Cr
1.63	2.90–2.99	4.73–4.87	...	Ag-As (9.8-15.1 at. % As)
1.63–1.64	2.92	4.76–4.79	...	Au-In (15.7-20.2 at. % In)
1.63	3.07–3.10	4.99–5.04	A3	$MgCd_{2-x}$
1.63	3.13	5.09	A3	$Cd(Mg, Al)_2$
1.63	3.21–3.17	5.21–5.15	A3	Mg-Al (2-11 at. % Al)
1.63	3.19	5.18	B4	GaN
1.63	3.21	5.20	A3	Mg-Mn (1.5 at. % Mn)
1.63	3.21	5.21	A3	Mg
1.63	3.35	5.46	...	Zr_2H
1.63	3.43	5.56	B8	$Cr_{1-x}S$
1.63	3.58	5.83	...	β-Al_2S_3
1.63	3.58	5.84	A3	He (1.45° K., 37 atm.)
(1.63)	(3.61)	(5.89)	...	ZrO_2
1.63	3.63	5.92	B8	FeSe
1.63	3.75	6.11	A3	Er
1.63	3.76	6.13	A3	H_2 (4° K.)
1.63	3.76	6.13	...	$ZnAl_2S_4$
1.63	3.80	6.19	C6	$ZrSe_2$
1.63	4.13	6.73	B4	γ-MnSe
1.63	4.20	6.86	B4	Cd(S, Se)
1.63	4.24	6.92	C14	$MnBe_2$
1.63	4.26	6.96	C14	$CrBe_2$
1.63	4.31	7.03	B4	CdSe
1.63	4.32	7.06	A3	β-Sr (521° K.)
1.63	4.36	7.10	C14	$ReBe_2$
1.63	4.40	7.14	C14	VBe_2
1.63	4.44	7.25	...	CH_3OH (165° K.)
1.63	4.47	7.29	...	H_2O (90° K.)
1.63	4.51	7.34	C10	H_2O (273° K.)
1.63	4.53	7.36	C10	D_2O (272° K.)
1.63	4.74	7.73	C41	Fe_2W
1.63	4.78	7.81	C14	Fe_2Ti
1.63	4.81	7.86	C14	Fe_2Ta
1.63	4.83	7.88	C14	Fe_2Cb
1.63	4.87	7.95	C14	Mn_2Ta
1.63	4.96	8.08 × 2	C14	Mn_2Ti
1.63	5.04	8.24	C10	SiO_2 (β-trydymite)
1.63–1.65	5.22–5.10	8.56–8.42	...	$MgZn_2$-MgCuAl (100-0 mole % $MgZn_2$)
1.63	5.11	8.32	$D0_{24}$	Ni_3Ti
1.63	5.14	8.39	C14	$ZrCr_2$
1.63	5.18	8.44	...	MgCuAl-$MgAl_2$
1.63	5.26	8.60	C14	$ZrRe_2$
1.63	5.43	8.85	$E9_2$	4BeO.$NaSbO_3$, swedenborgite
1.63	5.48	8.95	C14	$ThMn_2$
1.63	6.43	10.47	C14	$SrMg_2$
1.63	8.40	13.65	...	θ-Al_2O_3
1.63	9.00	14.70	...	Li_2SnO_3
1.64	2.66	4.34	...	Ni_2C
1.64	2.66	4.35	...	Co_2N
1.64–1.66	2.91–2.92	4.77–4.84	...	Cd-Au (25.3-35.5 at. % Cd)
1.64	2.91–2.93	4.78–4.81	...	Au_3Hg (18.8-32.4 at. % Hg)
1.64	3.68	6.02	...	β-Ga_2S_3
1.64	3.77	6.18	C6	VBr_2
1.64	3.82	6.25	B4	ZnS
1.64	3.83	6.27	C6	$MgBr_2$
1.64	3.97	6.50	A3	β-Ca
1.64	4.04	6.62	A3	β-N_2 (~40° K.)
1.64	4.06	6.66	B4	β-CuBr (664-743° K.)
1.64	4.14	6.80	C6	GeI_2
1.64	4.17	6.83	C6	MnI_2
1.64	4.44	7.29	C14	$MoBe_2$
1.64	4.45	7.28	C14	WBe_2
1.64	4.59	7.52	B4	AgI
1.64–1.65	4.87–4.82	7.81–7.97	C14	$Mg(Ni, Cu)_2$
1.64	4.82	7.91		$FeTa_2$
1.64	4.87	7.97	C14	Mn_2Cb
1.64	5.01	7.89	C14	$MgCu_{1.5}Si_{0.5}$
1.64	5.04	8.24	C14	Mn_2Zr
1.64	5.10	8.36	C14	MgCuAl-$MgCu_2$
1.64–1.65	5.14–5.22	8.44–8.62	C14	$Mg(Zn, Cu)_2$
1.64	5.15	(8.43) × 2	...	$Mg_3Zn_2Cu_2Al_2$
1.64	5.17	8.51	C14	$MgZn_2$
1.64	5.19	8.53	C14	$ZrOs_2$
1.64	5.29	8.66	C14	ZrV_2
1.64	6.26	10.25	C14	$CaLi_2$
1.64	6.93	11.35	...	β-Au-Be
1.64	7.50	12.29	C14	KNa_2
1.64	8.30	13.63	...	$(C_6H_5CO)_2$, benzil
1.64	22.19	36.34	...	$K(Fe, Al, Mg, Mn)_{10}(OH)_{12}[Si_2O_5]_6$, ferrostilpnomelane
1.65	2.55	4.20	...	Ni-Mo (25.0 at. % Mo)
1.65	3.56	5.88	C6	$TiCl_2$
1.65	3.75	6.18	C6	$FeBr_2$
1.65	4.07	6.74	...	β-CO (~61° K.)
1.65	4.31	7.09	B4	β-CuI (675–713° K.)
(1.65)	4.82	(7.97) × 2	C36	$MgNi_2$
(1.65)	4.87–4.82	(8.05–7.97) × 2	C36	$Mg(Ni, Zn)_2$
(1.65)	5.10	(8.40) × 2	C36	MgCuAl
1.65	5.20–5.22	8.60–8.62	C14	$Mg(Zn, Ni)_2$
1.65	5.67	9.35	...	K_2MnF_6
1.65	5.75	9.5	...	$2Ca(OH)_2.Al(OH)_2ClO_4$
1.65	5.75	9.51	...	K_2PdF_6
1.66–1.68	3.44–3.46	5.69–5.80	B8	$Fe_{0.83-0.96}S$
1.66	3.45	5.71	B8	CrS
1.66	3.49	5.78–5.79	...	Pb-Bi (20-50 at. % Bi)
1.66	3.70	6.13	C6	$CoBr_2$
1.66	4.11	6.82	C6	TiI_2
1.66	4.15	6.89	C6	MgI_2
1.66	5.14	8.51	C14	$ZrRu_2$
1.66	9.94	16.51	$D2_2$	$MgZn_5$
1.66	10.02	16.61	R32	$K_3Cu(CN)_4$
1.67	2.91	4.72	...	Ag_3Al (843° K.)
1.67	3.41	5.70	C6	TiS_2
1.67	3.59	5.99	B8	VSe
1.67	3.83	6.39	B8	TiTe
1.67	4.00	6.67	C6	VI_2
1.67	4.05	6.76	C6	FeI_2
1.67	5.75	9.6	...	$2Ca(OH)_2.Al(OH)_2MnO_4$
1.68	3.45	5.81	B8	FeS
1.68	3.97	6.66	C6	CoI_2
1.68	5.14	8.62	$H1_4$, $H2_8$	$KLiSO_4$
1.68	5.17	8.67	$H2_8$	$KAlSiO_4$, kalsilite
1.68	5.22	8.78	$H2_8$	$BaAl_2O_4$
1.68	5.45	9.13	R3*m*	KNO_3 (398° K.)
1.68	6.71	11.28	...	Bi_2Se_3
1.69	4.72	7.98	$H3_2$	$KAl(SO_4)_2$
1.69	3.54	5.99	C6	$TiSe_2$
1.70	3.16	5.37	C6	$NiCl_2.3Ni(OH)_2$
1.70	4.75	8.05	$H3_2$	$KCr(SO_4)_2$
1.70	9.43	16.00	...	$(Mn, Mg, Na)Be_2Fe_2(PO_4)_4.6H_2O$, faheyite
(1.71)	(3.23)	(5.51)	C6	$CoCl_2.3Co(OH)_2$
1.71	3.28	5.60	C6	$Co(^1/_3Cl, {}^2/_3Br)_2.3Co(OH)_2$
1.71	4.01	6.83	Ce_2O_2S	Ce_2O_2S
1.71	4.04	6.89	Ce_2O_2S	La_2O_2S
1.71	7.20	12.32	$O2_5$	$C(NH_2)_3I$
1.72	4.24	7.27	P6/*mmm*	Cu_2Te
1.72	4.84	8.33	$H3_2$	$NH_4Fe(SO_4)_2$
1.72	22.0	37.85	...	$K(Al, Fe, Mg, Mn)_{10}(OH)_{12}[Si_2O_5]_6$, stilpnomelane
1.73	3.36	5.81	B8	VS
1.73	3.41	5.91	C6	TaS_2
1.73	3.77	6.51	C6	$TiTe_2$
1.73	3.93	6.77	Ce_2O_2S	Pu_2O_2S
(1.73)	(4.23) × 7	7.33	...	$TiBe_{12}$
1.73	22.5	39.1	...	$3MnO.4SiO_2.4H_2O$, parsettensite
1.74	3.80	6.59	...	YC_2
1.74	4.73	8.25	$H3_2$	$NH_4Al(SO_4)_2$
1.74	5.33	9.26	...	$FeSn_2$
1.74	5.75	10.0	...	$2Ca(OH)_2.Al(OH)_2.^1/_2CrO_4.nH_2O$
1.74	8.25	14.34	P3$_c$1	$Cu_6AlSO_4(OH)_{12}Cl.3H_2O$, spangolite
1.75	3.56	6.22	B8	TiSe

Table V. Hexagonal Substances Tabulated According to Axial Ratios (*Continued*)

c/a	a, A.	c, A.	Type	Substance
1.75	4.20	7.42	$D0_6$	$PbThF_6$
1.75	4.28	7.48	$D0_6$	$BaUF_6$
1.75	4.79	8.39	$H3_2$	$NH_4Cr(SO_4)_2$
1.75	9.50	16.60	...	Na_2SnO_3
(1.75)	(9.92)	(17.34)	...	Na-cellulose II
1.76	4.19	7.35	$D0_6$	$PbUF_6$
1.76	4.27	7.53	$D0_6$	AcF_3
1.76	4.29	7.54	$D0_6$	$BaThF_6$
1.76	14.33	25.15	$P\bar{3}1c$	Tl_2Cl_3
1.77	4.09	7.24	$D0_6$	PuF_3
1.77	4.11	7.27	$D0_6$	NpF_3
1.77	4.14	7.33	$D0_6$	UF_3
1.77	4.27	7.60	$D0_{18}$	Li_3P
1.77	4.71	8.33	$D0_{18}$	α-Li_3Sb
1.77	4.99	8.82	$D0_{18}$	Na_3P
1.77	5.10	9.00	$D0_{18}$	Na_3As
1.77	5.37	9.52	$D0_{18}$	Na_3Sb
1.77	5.46	9.68	$D0_{18}$	Na_3Bi
1.77	5.79	10.24	$D0_{18}$	K_3As
1.77	6.19	10.95	$D0_{18}$	K_3Bi
1.78	4.07	7.23	$D0_6$	AmF_3
1.78	4.40	7.83	$D0_{18}$	Li_3As
1.78	4.87	8.65	$D0_{18}$	Mg_3Hg
1.78	6.04	10.71	$D0_{18}$	K_3Sb
1.78	6.04	10.72	$D0_{18}$	K_3(Sb, Te)
1.78	4.04	7.19	$D0_6$	$CaThF_6$
1.78	4.11	7.30	$D0_6$	$SrUF_6$
1.78	4.14	7.34	$D0_6$	$SrThF_6$
1.78	11.3	20.1	...	$C_6H_3(COOC_2H_5)_3$, triethyl-1,3,5-benzene tricarboxylate
1.79	5.75	10.3	...	$2Ca(OH)_2.Al(OH)_3IO_3.2.9H_2O$
1.79	5.75	10.3	...	$2Ca(OH)_2.Al(OH)_2.{}^1/_2WO_4.nH_2O$
1.80	4.05	7.30	$D0_6$	$ThOF_2$
1.80	5.40	9.70	...	KNO_3 (425° K.)
1.80	11.30	20.29	...	$K_3Rh(C_2O_4)_3.H_2O$
1.81	3.65	6.61	C6	$CdI_{0.5}(OH)_{1.5}$
1.81	5.75	10.4	...	$2Ca(OH)_2.Al(OH)_2.{}^1/_2S_2O_3.nH_2O$
1.82	4.64	8.46	$D0_{18}$	$AuMg_3$
1.82	6.34	11.56	Kl_2	$Cs_2S_2O_6$
1.83	3.24	5.92	C6	$CoBr_2.3Co(OH)_2$
1.83	3.36	6.13	C6	VSe_2
1.84	3.18	5.83	C6	$NiBr_2.3Ni(OH)_2$
1.84	4.47	8.21	$O3_1$	C_2H_6 (100° K.)
1.84	6.80	12.48	...	Ni_5As_2
1.84	7.18	13.22	...	$RbC_2H_4O_6$, Rb tartrate
1.85	2.41	4.45	...	$CoMn_3$
1.85	3.03	5.59	...	CbN
1.86	2.67	4.95	A3	Zn
1.86	2.67	4.96	A3	Zn-Cd (1 at. % Cd)
1.86	2.67	4.97–4.98	A3	Zn-Al (0-5.0 at. % Al)
(1.86)	6.84	(12.72)	...	$2(CaSO_4).\sim 1H_2O$
1.87	2.67	4.97–4.99	A3	Hg-Zn (1.51-5.87 at. % Hg)
(1.88)	(2.94)	(5.53)	$D0_{19}$	$MgCd_3$
1.88	5.75	10.8	...	$2Ca(OH)_2.Al(OH)_2.{}^1/_2Fe(CN)_6$
1.89–1.90	2.96–2.97	5.60–5.64	...	Mg-Cd (45-0 at. % Mg)
1.89–1.93	2.98–2.97	5.62–5.72	...	Hg-Cd (4.3-29.1 at. % Hg)
1.89	2.98	5.62	A3	Cd
1.89	11.18	21.04	R3	$Na_2B_4O_7.5H_2O$, tinkalconite
1.91	3.01	5.72	C6	Ag_2F
1.91	4.55	8.71	$(D4_1)$	B_2H_6
1.91	5.24	10.00	$J1_{12}$	$NaSbF_4(OH)_2$
1.92	4.33	8.32	...	B_2O_3
1.93	6.33	12.21	$F5_1$	$CsICl_2$
1.94	3.48	6.74	A10	Hg (177° K.)
1.94	5.39	10.46	B22	RbSeH
1.95–1.97	5.98–5.97	11.66–11.77	...	$Fe_{1-x}S$, $x = 0.025$
1.96	6.53	12.78	$J1_2$	$K_2Sn(OH)_6$
1.98–1.99	9.40	18.59–18.72	...	$3Mn_2O_3.MnSiO_3$, braunite
1.99	5.15	10.24	B22	KSeH
1.99	5.17	10.30	B22	RbSH
2.00	6.41	12.85	$J1_2$	$K_2Pt(OH)_6$
2.01	4.96	9.95	B22	KSH
2.01	8.20	16.45	$P6_3/mmc$	KU_6F_{25}
2.02	2.71	5.47	...	Zn-Hg (25-50 at. % Hg)
2.02	8.34	16.81	$P6_3/mmc$	KTh_6F_{25}
2.02	10.50	21.23	$P6_3/m$	$KNa_{22}(SO_4)_9(CO_3)_2Cl$, hanksite
2.05	4.47	9.16	B22	NaSH
2.05	4.66	9.54	B22	NaSeH
2.07	5.91	12.21	R3	$Ag_2H_3IO_6$
2.07	7.46	15.45	...	$AgIO_3$
2.10	7.86	16.52	R3c	NiO.3BaO
(2.11)	5.06	(11.24)	(C8)	$AlAsO_4$
2.11	14.34	30.21	R3m	(Na, Ca, Fe)$_6$ZrSi$_6$O$_{18}$-(OH, Cl), eudialyte
2.12	6.84	14.50	...	$Co_2(OH)_3Cl$
2.13	5.27	11.25	...	β-$LiAlSiO_4$, eucryptite
2.14–2.15	9.68–9.60	20.70–20.62	R3m	$PbSO_4.K_2SO_4$, palmierite
2.16	5.61	12.14	...	B_4C
2.17	6.90	15.0	...	$CdSO_4.3.5Cd(OH)_2$
2.19	3.18	6.97	C6	$Co(NO_3)_2.3Co(OH)_2$
2.19	6.01	13.16	...	$NaIO_4.3H_2O$
2.21	5.74	12.7	...	$2Ca(OH)_2.Al(OH)_2.OC_6H_2(NO_2)_3.nH_2O$, picrate
2.22	4.93	10.93	C8	$AlPO_4$, berlinite
2.26	7.17	16.19	$K7_1$	$K_3W_2Cl_9$
2.26	7.17	16.19	$K7_1$	$(NH_4)_3W_2Cl_9$
2.27	7.19	16.33	Alunite	$NaFe_3(SO_4)_2(OH)_6$
2.27	7.23	16.43	Alunite	$AgFe_3(SO_4)_2(OH)_6$, argentojarosite
2.27	11.58	26.33	...	Poly(γ-methyl L-glutamate)
2.29	4.16	9.52	B9	HgS
2.29	10.86	24.87	R3̄	$Na_9K_3Fe(SO_4)_6(OH)_2.9H_2O$, ungemachite
2.30	5.48	12.62	...	Cd-Au (45.5 at. % Cd)
2.30	67.1	154.0	...	Pepsin
2.31	6.99	16.13	R3m	$Ca_2Al_2(PO_4)_2(OH)_4.H_2O$, deltaite
2.31	6.99	16.13	R3m	$CaAl_3(PO_4)_2(OH)_5.H_2O$, pseudo wavellite
2.32	7.16	16.36	$K7_1$	$Tl_3W_2Cl_9$
2.32	7.36	17.09	$K7_1$	$Cs_3W_2Cl_9$
2.34	6.97	16.29	...	$CaAl_3(SO_4)(PO_4)(OH)_6$, woodhouseite
(2.34)	7.21	(16.83)	Alunite	$PbFe_3(SO_4)_2(OH)_6$
2.34	7.25	16.98	$K7_1$	$Rb_3W_2Cl_9$
2.36	7.17	16.93	Alunite	$Fe_3(SO_4)_2(OH)_5.2H_2O$
2.36	7.21	17.03	Alunite	$KFe_3(SO_4)_2(OH)_6$, jarosite
2.36	7.21	17.03	Alunite	$NH_4Fe_3(SO_4)_2(OH)_6$
2.37	6.98	16.55	R3̄m	$SrAl_3(PO_4)_2(OH)_5.H_2O$, hamlinite
2.38	5.96	14.20	$J1_2$	$Na_2Sn(OH)_6$
2.38	7.39	17.58	$F5_{10}$	$KAg(CN)_2$
2.41	6.96	16.8	R3̄m	$SrAl_3(SO_4)(PO_4)(OH)_6$, svanbergite
2.42	5.72	13.86	...	(Zn, Mg, Fe^{II})(Sn, Zn)$_2$-(Al, Fe^{III})$_{12}O_{22}(OH)_2$, nigerite
2.44	2.96	7.22	...	NiO
(2.45)	(5.58) × 2	13.65	...	$Ni_3Pb_2S_2$, shandite
2.45	5.74	14.05	$P6_3/mmc$	$BaTiO_3$
2.46	5.71	14.02	...	$Ba(Ti_{0.75}Pt_{0.25})O_3$
2.46	6.46	15.92	$F4_1$	$Fe_2(CO)_9$
2.48	16.26	40.28	R3̄m	$ThSiW_{12}O_{40}.30H_2O$
2.49	16.16	40.28	R3̄m	$ThSiW_{12}O_{40}.27H_2O$
2.50	6.96	17.41	Alunite	$KAl_3(SO_4)_2(OH)_6$
2.50	7.19	18.01	...	$CsCuCl_3$
2.50	15.59	38.98	R3̄m	$Li_3HSiW_{12}O_{40}.24H_2O$
2.51	3.12	7.8	...	α-$Zn(OH)_2$
2.51	6.13	15.37	...	$Mg_6Al_2(OH)_{16}CO_3.4H_2O$, manasseite
2.51	6.21	15.60	...	$Mg_6Fe_2(OH)_{16}CO_3.4H_2O$, sjögrenite
2.51	7.05	17.66	...	$Ba(NO_2)_2.H_2O$
2.52	6.18	15.55	...	$Mg_6Cr_2(OH)_{16}CO_3.4H_2O$, barbertonite
2.53	4.92	12.48	$D0_{14}$	AlF_3
2.53	5.27	13.3	$P6_222$	Mg_2Ni
2.54	7.10	18.23	$P\bar{6}c2$	(Ce, La, ...)$Ca(CO_3)_2F$, synchysite
2.54	15.61	41.40	...	$(CrHSiW_{12}O_{40}.24H_2O)$
2.55	15.63	39.86	R3m	$H_3PW_{12}O_{40}.24H_2O$
2.55	15.63	39.88	...	$(FeHSiW_{12}O_{40}.24H_2O)$
2.56	5.22	13.35	$D0_{12}$	FeF_3
2.59	3.10	8.0	...	α-$Co(OH)_2$
2.59	5.17	13.40	$D0_{12}$	VF_3
2.60	3.09	8.0	...	α-(Co, Zn)$(OH)_2$
2.61	4.55	11.86	A7	Bi
2.62	4.30	11.26	...	ϵ-Cu-Sb
2.62	4.30	11.28	A7	Sb
2.62	4.54	11.87	...	Bi_3Sn
2.62	5.07	13.30	$D0_{12}$	CoF_3
2.63	15.63	41.18	R3̄m	$Zn_2SiW_{12}O_{40}.27H_2O$
2.64	5.14	13.58	$D5_1$	TiO_3
2.64	5.30	14.01	$P6_3cm$	$(Mg_{1.6}Al_{1.6}Fe_{0.4})[SiAlO_5]$-$(OH)_4$, amesite
2.64	15.59	41.18	R3̄m	$Li_3HSiW_{12}O_{40}.26H_2O$
2.64	15.67	41.30	R3̄m	$Cu_2SiW_{12}O_{40}.27H_2O$
2.65	15.47	41.00	R3m	$Ca_2SiW_{12}O_{40}.26H_2O$
2.65	15.61	41.40	...	$CrHSiW_{12}O_{40}.28H_2O$
2.65	15.63	41.44	...	$FeHSiW_{12}O_{40}.28H_2O$
2.66	2.52	6.69	B12	BN
2.67	3.08	8.2	...	α-(Ni, Zn)$(OH)_2$
2.67	8.20	21.99	R3c	$(C_6H_9(OH)_3.2H_2O)$, α-phloroglucitol
2.67	15.59	41.43	...	$AlHSiW_{12}O_{40}.28H_2O$
2.68	15.26	40.93	R3m	$Ba_2SiW_{12}O_{40}.24H_2O$
2.69	15.31	41.16	...	$Ba_3(PO_4.12WO_3)_2.48H_2O$
2.70	5.12	13.85	$E2_2$	$LiCbO_3$
2.71	4.96	13.42	$D5_1$	α-Ga_2O_3
2.71	5.11	13.83	$D5_1$	Rh_2O_3
2.73	4.76	13.0	$D5_1$	α-Al_2O_3
2.73	4.99–4.79	13.64–13.09	$D5_1$	(Al, $Fe)_2O_3$ (15-85 mole % Al_2O_3)
2.73	12.2	33.4	...	Tri-*l*-cyclohexanediamine cobaltic chloride tetrahydrate
2.74	2.30	6.27	...	$CdBr_2$
2.74	2.46	6.75	A9	C, graphite
2.74–2.75	4.78–4.93	13.08–13.55	$D5_1$	(Al, $Cr)_2O_3$ (15-85 mole % Cr_2O_3)

Table V. Hexagonal Substances Tabulated According to Axial Ratios (*Continued*)

c/a	a, A.	c, A.	Type	Substance
2.74	5.01–4.98	13.71–13.65	$D5_1$	$(Fe, Cr)_2O_3$ (25-75 mole % Cr_2O_3)
2.74	5.03	13.77	$D5_1$	Fe_2O_3
2.74	5.05	13.85	$E2_2$	$NiTiO_3$
2.74	6.10	16.71	$R\bar{3}$	WCl_6
2.75	4.95	13.61	$D5_1$	Cr_2O_3
2.76–2.78	5.09–5.05	14.06–14.03	...	$(Ti, Fe)_2O_3$ (50-75 mole % Fe_2O_3)
2.75	7.50	20.65	$D0_5$	BiI_3
2.76	5.05	13.93	$E2_2$	$MgTiO_3$
2.76	5.09	14.06	$E2_2$	$FeTiO_3$, ilmenite
2.77	5.05	13.72	$E2_2$	$CoTiO_3$
2.77	5.76	15.9	...	NH_4NO_3(V) (<255° K.)
2.78	6.42	17.83	...	α-Al_2S_3
2.79	4.89	13.65	$D0_{12}$	RhF_3
2.79	6.39	17.82	$D0_5$	$ScCl_3$
2.79	7.50	20.93	$D0_5$	SbI_3
2.79	(8.89)	(24.80)	...	$Be_4O(CH_3COO)_6$, Be oxyacetate
2.80	3.77	10.56	A7	As
2.80	5.14	14.36	$E2_2$	$MnTiO_3$
2.80	5.27	14.7	...	$Pb(OH)_2$
2.81	2.45	6.85	...	CdI_2
2.81	3.67	10.29	$E0_3$	Cd(OH)Cl
2.81	5.06	14.24	$D0_{12}$	PdF_3
2.82	4.94	13.95	$D5_1$	V_2O_3
2.82	4.96	13.98	$E2_2$	$Fe_{1-x}Ti_{1+x}O_3$ (44.5% FeO)
2.84	5.26	14.94	$E2_2$	$CdTiO_3$
2.86	6.12	17.54	$D0_5$	$TiCl_3$
2.87	6.05	17.38	$D0_5$	$FeCl_3$
2.87	6.42	18.40	$D0_5$	$FeBr_3$
2.88	6.46	18.64	$D0_5$	$TiBr_3$
2.89	3.43	9.92	...	$CdF_2.(4\text{-}6)Cd(OH)_2$
2.89	3.77	10.89	A7	As-Sn (70.9 at. % As)
2.89	5.10	14.72	P6/mmm	$CaAl_2Si_2O_8$
2.89	6.02	17.38	$D0_5$	VCl_3
2.90	5.99	17.38	$D0_4$	$CrCl_3$
2.90	6.86	19.88	...	CrI_3
2.91	6.29	18.30	$D0_5$	$CrBr_3$
2.92–2.94	6.23–6.15	18.19–18.08	...	Cr(Br, Cl)3, mole fr. Br = 0.55 to 0.75
2.94	6.06	17.82	...	$CrBrCl_2$
2.94	6.52	19.14	...	$CrIBr_2$
2.94	7.63	22.42	$R\bar{3}$	$K_4Ni(NO_2)_6$
(2.97)	(5.92)	(17.56)	$D0_{1b}$	$AlCl_3$
2.97	7.19	21.38	$D0_5$	AsI_3
2.99	4.34	12.96	$P6_3/mmc$	Pt_2Sn_3
3.00	5.35	15.98	$E2_2$	$NaSbO_3$
3.00	6.24	18.70	...	$CrICl_2$
3.08	5.13	15.80	...	$BeCO_3.4H_2O$
3.08	7.15	22.06	$OH6_2$	$(NH_3CH_3)_2SnCl_6$
3.19	6.87	21.96	$OH6_2$	$(NH_3CH_3)_2PtCl_6$
3.21	5.72	18.38	$P6_322$	$Be_4Mg_3Al_{16}O_{32}$, taaffeite
3.22–4.71	4.25–3.99	13.70–18.78	C27	$CdBr_2$-CdI_2
3.22	4.25	13.70	C27	CdI_2
3.22	4.76	15.30	$G0_1$	$ScBO_3$
3.22	9.3	30.1	...	$N(C_2H_4.NH_3Cl)_3HCl.nH_2O$
3.23	4.64	14.98	$G0_1$	$ZnCO_3$
3.24	4.08	13.23	...	$BaBiO_2Br$
3.24	4.44	14.39	$R\bar{3}m$	$N_2H_6F_2$
3.24	4.60	14.91	$G0_1$	$MgCO_3$
3.24	4.66	15.08	$G0_1$	$CoCO_3$
3.24	4.78	15.49	$G0_1$	$InBO_3$
3.25	4.68	15.23	$G0_1$	$LiNO_3$
(3.26)	(2.56)	8.32	$D0_{24}$	Ni_3Ti
3.26	4.73	15.40	C36	Ti_2Co
3.26	4.73	15.42	C36	Co_2Ta
3.26	4.74	15.46	C36	Co_2Cb
3.26	4.96	16.15	C36	Fe_2Zr
3.26	4.96	16.15	C14	Mn_2Ti
3.27	3.08	10.08	B5	SiC-(4H)
3.27	3.81	12.45	B5	ZnS, wurtzite-(4H)
3.27	4.91	16.07	$G0_1$	$(Cd, Mn)CO_3$ (25 mole % $CdCO_3$)
3.28	3.85	12.6	...	$Cu_3Fe_2SnS_6$, stannite
3.28	4.68	15.36	$G0_1$	$FeCO_3$
3.28	4.86	15.95	$G1_1$	$CaSn(BO_3)_2$
3.29	4.75	15.65	$G0_1$	$MnCO_3$
3.29	4.82	15.86	C36	$MgNi_2$
3.29	4.93	16.22	$G0_1$	(Cd, Mn) CO_3 (50 mole % $CdCO_3$)
3.29	4.93	16.22	$G0_1$	(Mn, Ca) CO_3 (75 mole % $MnCO_3$)
3.29	4.95	16.28	$G0_1$	(Cd, Mn) CO_3 (75 mole % $CdCO_3$)
3.29	4.96	16.33	$G0_1$	$CdCO_3$
3.30	6.87	22.7	$P6_322$	$Fe_{0.97}S$, pyrrhotite
3.31	4.84	16.02	$G1_1$	$CaMg(CO_3)_2$
3.32	5.06	16.81	$G0_1$	$NaNO_3$
3.33	4.96	16.53	...	$Na_2Mg(CO_3)_2$
3.34	4.83	16.15	$G1_1$	Ca(Mg, Fe)$(CO_3)_2$, ankerite
3.39	4.97	16.83	$G0_1$	(Ca, Cd)CO_3 (75 mole % $CaCO_3$)
3.40	4.96	16.85	$G0_1$	(Ca, Mn)CO_3 (12.5 mole % $MnCO_3$)
3.40	5.07	17.25	$G0_1$	YBO_3
3.40	5.3	18.25	$E2_2$	$KSbO_3$
3.42	4.99	17.06	$G0_1$	$CaCO_3$
3.46	5.29	18.33	...	$CuMg_2$
3.53	4.95	17.49	...	KC_{16}
3.54	6.33	22.4	...	$3Zn(OH)_2.2Zn(OH)Br$
3.58	8.44	30.19	R3c	$Na_2Li(SO_4)_2.6H_2O$
3.59	10.31	37.0	$R\bar{3}c$	$Ca_3(PO_4)_2$, whitlockite
3.63	4.95	17.99	...	RbC_{16}
3.67	5.39	19.79	...	$Sr_3(PO_4)_2$
3.67	5.8	21.3	R3m	$K_2MnO_4CrO_4$
3.72	6.34	23.60	R3m	$ZnCl_2.4Zn(OH)_2$
3.73	4.21	15.72	$R\bar{3}m$	UO_2F_2
3.73	5.54	20.69	...	$PbK_2(SO_4)_2$, palmierite
3.74	2.93	10.97	$P6_3/mmc$	γ'-Mo-C
3.75	4.95	18.55	...	CsC_{16}
3.75	5.60	21.00	R3m	$Ba_3(PO_4)_2$
3.89	(4.47)	(17.39)	...	β-$(CH_2O)_n$, β-polyoxymethylene
3.90–3.92	3.16	12.29–12.34	C7	$WS_{1.96-2.0}$
3.90	3.16	12.32	C7	MoS_2
3.91	6.07	23.74	...	$2(Pb, Mn)O.3Fe_2O_3$, magneto-plumbite
3.92	5.89	23.07	...	$PbO.6Fe_2O_3$
3.93	5.87	23.08	...	$SrO.6Fe_2O_3$
3.94	3.29	12.97	C7	WSe_2
3.94	5.53	21.79	...	$CaF_2.5Al_2O_3$
3.94	5.55	21.87	...	$CaO.6Al_2O_3$
3.94	5.57	21.93	...	(Ca, Mg, Mn)O.-5.8(Al, Ti)$_2O_3$
3.94	5.89	23.22	...	$BaO.6Fe_2O_3$
3.95	5.57	21.99	...	$SrO.6Al_2O_3$

no barium sulfate precipitate. A specific confirmation of the dithionate ion is obtained with the nickel ethylenediamine nitrate test (*15*). A bromine content of 21.7 weight % (based on the original sample) was determined by x-ray absorption using the characteristic bromine K-absorption edge. Subtracting the x-ray absorption for potassium bromide, one finds that the balance of the absorption at several wave lengths corresponds to 68 weight % potassium dithionate in the original powder. The confirmed analysis is thus reported at 68 weight % potassium dithionate and 32 weight % potassium bromide. (In completing the comparison of the identified pattern with the remaining hexagonal structures, one finds a partial intensity match for $S3_2$ at $c/a = 1.28$, $a = 9.8$ A., $c = 12.6$ A. No substance with these lattice constants is listed under $S3_2$.)

An alternative method of identifying the uncatalogued phase is based on the general tabulation of hexagonal substances in Table V. After ascertaining that the unidentified lines can be indexed hexagonal at $c/a = 0.64$ with $a = 9.80$ A. and $c = 6.29$ A., one searches in Table V for these lattice constants and finds potassium dithionate listed with $c/a = 0.643$, $a = 9.80$ A., and $c = 6.30$ A. As in the previous case, confirmatory tests are required to support the phase identification. When searching through Table V it is advisable to look not only under a particular value of c/a but also under $\frac{r}{\sqrt{p^2 + q^2 + pq}}\, c/a$ where $r = 1,2\ldots$, n; $p,q = 0,1,2,\ldots n$ but $p + q \neq 0$. In practice one normally considers only the factors 2, $\frac{2}{\sqrt{3}}$, $\frac{1}{\sqrt{3}}$, and $\frac{1}{2}$.

The data of Table III suggests how one can expedite the indexing of hexagonal powder patterns. Reflections {110} and {300} are not ruled out by any general space group criteria. It is experimentally observed that for approximately 60% of the hexagonal substances it is possible to pick out the {110} and {300} reflections by translating the log d strip of the unknown pattern along the {*hko*} scale at the top of Figure 1. To apply this method to the above case, one fixes the first unidentified line, $d_1 = 6.30$ A., on point {110} of the {*hko*} scale and notes if any of the remaining d's coincide with {300}. As no match is found, one proceeds to the second line and observes that $d_2 = 5.10$ A. and $d_6 = 2.95$ A. coincide with {110} and {300}, respectively. However, on following the {110} line down the logarithmic charts, one is unable to index satisfactorily the remaining lines unless one permits unreasonably large lattice constants. With the third line (4.91 A.) as {110}, one finds a coincidence at {300} with $d_8 =$

Table V. Hexagonal Substances Tabulated According to Axial Ratios (*Continued*)

c/a	a, A.	c, A.	Type	Substance
3.98	11.88	47.24	...	$PbO.2Fe_2O_3$, plumboferrite
4.00	5.93	23.73	$D5_6$	$K_2O.11Fe_2O_3$
4.02	5.59	22.50	$D5_6$	$Na_2O.11Al_2O_3$
4.03	5.93	22.88	$D5_6$	$Rb_2O.11Fe_2O_3$
4.04	3.50	14.12	$F5_{11}$	NaFHF
4.05	3.68	14.88	$F5_{11}$	$CaCN_2$
4.06	5.59	22.67	$D5_6$	$(K, Na)_2O.11Al_2O_3$
4.06	5.59	22.72	$D5_6$	$K_2O.11Al_2O_3$
4.07	5.59	22.72	...	$BaO.(5\text{-}6)Al_2O_3$
4.09	2.46	10.06	$R\bar{3}m$	C, graphite
4.18	3.64	15.20	$F5_{11}$	NaN_3
4.22	3.59	15.13	$F5_{11}$	NaCNO
4.31	10.53	45.49	...	$Na_2Ce(Mn, Ta, Fe)H_2[(Si, P)O_4]_3$, steenstrupine
4.32	3.79	16.36	B18	CuS
4.32	4.95	21.38	...	KC_8
4.32	8.92	38.5	...	$C_{32}H_{30}ON_4Mg.CO_2CH_3.COOC_2H_5.H_2O$, ethylchlorophyllide
4.38	3.94	17.25	B18	CuSe
4.41	8.27	36.50	$R\bar{3}$	$Mn_{10}Mg_2Al_3(AsO_4)_3(OH)_{24}$, hematolite
4.41	4.28	18.23	C19	Cs_2O
4.45	(4.10)	18.24	$(P6_3/mmc)$	$(Ce, La, ...)Ca(CO_3)_2F$ synchisite
4.50	12.83	57.7	...	δ_1-Zn-Fe (90 at. % Zn)
4.51	3.88	17.50	$R\bar{3}m$	$Ca(UO_2)O_2$
4.54	3.86	17.50	C19	$CdCl_2$
4.56	4.54	20.7	...	PbI_2(II)
4.59	3.60	16.53	C19	$3CdCl_2.5Cd(OH)_2$
4.60	4.95	22.78	...	RbC_8
4.61	3.99	18.37	$R\bar{3}m$	$Sr(UO_2)O_2$
4.65	2.98	13.87	$P6_3/mmc$	B_5W_2
4.67	7.21	33.67	$R3m$	$PbFe_8(SO_4)_2(OH)_6$
4.69	2.98	13.98	...	B_5Ti_2
4.71	3.78	17.82	C19	$ZnCl_2$
4.75	3.69	17.51	C19	$MnCl_2$
4.76	3.96	18.80	C19	$CdBr_2$
4.78	3.39	16.20	$F5_{11}$	$RbCrS_2$
4.78	3.93	18.77	C19	$ZnBr_2$
4.81	4.95	23.81	...	CsC_8
4.84	4.24	20.52	$P\bar{3}m1$	CdI_2(III)
4.90	3.08	15.12	B6	SiC-(*6H*)
4.90	3.55	17.36	C19	$NiCl_2$
4.90	3.56	17.44	C19	$CoCl_2$
4.90	3.58	17.55	C19	$FeCl_2$
4.90	3.59	17.58	C19	$CdBr_{0.6}(OH)_{1.4}$
4.90	3.60	17.63	C19	$MgCl_2$
4.90	3.82	18.71	B6	ZnS, wurtzite-(*6H*)
4.93	3.73	18.34	C19	$NiBr_2$
4.96	6.15	30.5	...	$CaCO_3.H_2O$
4.97	3.82	18.97	$R\bar{3}m$	YOF
4.98	4.06	20.21	$R\bar{3}m$	LaOF
5.04	3.91	19.67	C19	NiI_2
5.20	3.28	17.02	...	NiCl(OH)
5.24	4.36	22.8	$(G7_1)$	$BaCO_3.2(Ce, La, ...)FCO_3$, cordylite
5.27	3.03	15.96	$F5_{11}$	$NaFeO_2$
5.34	10.77	57.51	$R\bar{3}m$	$Cu_{18}Al_2(AsO_4)_3(SO_4)_3(OH)_{27}.36H_2O$, chalcophyllite
5.41	4.74	25.63	$D8_5$	Co_7W_6
5.41	4.75	25.68	$D8_5$	Fe_7Mo_6
5.43–5.61	4.76–4.75	25.83–26.88	$D8_5$	$Fe_{7+x}W_{6-x}$
5.47	3.71	20.29	$F5_{11}$	$NaCrSe_2$
5.55	3.53	19.57	$F5_{11}$	$NaCrS_2$
5.64	3.04	17.12	$F5_{11}$	$CuFeO_2$
5.66	5.3	30.1	...	$K(Mg, Fe, ...)_3(OH, F)_2[(Al, Si)_2O_5]_2$
5.74	2.98	17.10	$F5_{11}$	$CuCrO_2$
5.86	3.62	21.20	$F5_{11}$	$KCrS_2$
6.09	6.04	36.8	O7	$C(CH_2O)_4(CHC_6H_5)_2$, dibenzalpentaerythritol
6.54	3.08	20.15	$P6_3mc$	SiC-(*8H*)
6.59	3.29	21.64	$E9_4$	Al_2C_3N
6.72	3.17	21.29	$S5_7$	$Fe_4^{II}Fe_2^{III}(OH)_8[Fe_2^{III}Si_2O_{10}]$, cronstedtite
6.82	4.10	27.99	$(G7_1)$	$CaCO_3.2(Ce, La, ...)FCO_3$, parisite
6.82	4.77	34.1	$P3m1$	$C_{12}H_{25}OH$, 1-dodecanol
6.95	3.01	20.93	$R\bar{3}m$	B_5Mo_2
6.95	4.32	30.07	C33	Bi_2Te_2S, tetradymite
6.96	4.37	30.42	C33	Bi_2Te_2
6.98	4.77	33.3	...	$C_{24}H_{50}$, *n*-tetracosane, 320° K.
7.03	3.44	24.2	$(F5_1)$	$K_{0.5}CrSe_2$
7.08–7.20	3.98	28.12–28.65	$R\bar{3}m$	Bi_2O_3-SrO (14-26% Sr)
7.15	4.25	30.4	...	Sb_2Te_3
7.51	3.33	24.98	$D7_1$	Al_4C_3
7.51	6.19	46.47	...	$Mg_6Cr_2(OH)_{16}CO_3.4H_2O$, stichtite
7.52	6.20	46.6	...	$Mg_6Fe_2(OH)_{16}CO_3.4H_2O$, pyroaurite
7.53	6.14	46.24	...	$Mg_6Al_2(OH)_{16}CO_3.4H_2O$, hydrotalcite
7.75	3.16	24.4	...	$CoCl(OH).4Co(OH)_2.4H_2O$
7.84	3.43	26.9	$F5_{11}$	$RbCrSe_2$
7.85	3.89	30.53	C12	$CaSi_2$
7.87	3.06	24.0	...	$NiCl_2.6\text{-}7Ni(OH)_2.xH_2O$
7.89	3.14	24.8	...	$4Co(OH)_2.CoBr(OH)$
7.89	3.14	24.8	...	$4Zn(OH)_2.Zn(OH)_{0.7}(Br, Cl)_{1.3}$
7.93	3.06	24.2	...	$NiBr_2.7Ni(OH)_2.xH_2O$
7.98	4.14	28.6	...	Bi_2Se_3
8.18	3.08	25.18	$P3m1$	SiC-(*10H*)
(8.37)	(5.14)	(43.00)	$S5_4$	$Al_2(OH)_4(Si_2O_5)$
8.82	4.09	36.05	...	Sn_3As_2
9.29	4.8	44.7	...	$C_{16}H_{33}OH$, *n*-hexadecyl alcohol
9.36	4.24	39.7	$R3m$	Bi_4TeS_2, joseite
9.67	4.11	39.75	...	CdBrI
9.82	3.67	36.0	...	$MgAl_2S_4$
9.82	3.68	36.15	...	$MnAl_2S_4$
9.84	3.63	35.65	...	$FeAl_2S_4$
10.70	5.41	57.9	...	$C_6H_{12}O_4N_2S_2$, *l*-cystine
12.23	3.83	46.84	B7	ZnS, wurtzite-(*15R*)
12.28	3.08	37.82	B7	SiC-(*15R*)
13.42	4.08	54.7	...	Bi_2Se_3, paraguanajuatite
13.66	9.72	13.28	...	$Ca_4(Si_6O_{16})(OH)_2.3H_2O$, gyrolite
15.54	3.08	47.85	$P3m1$	SiC-(*19H*)
17.17	3.08	52.89	$R3m$	SiC-(*21R*)
22.08	3.08	68.00	$R3m$	SiC-(*27R*)
26.98	3.08	83.10	$R3m$	SiC-(*33R*)
41.88	3.08	129.0	$R3m$	SiC-($51R_{(a)}$), ($51R_{(b)}$)
61.32	3.08	188.9	$R3m$	SiC-(*75R*)
68.68	3.08	211.4	$R3m$	SiC-(*84R*)
71.14	3.08	219.1	$R3m$	SiC-(*87R*)

2.82 A.—i.e., $d_3:d_8 = 4.91:2.82 = 1.74 \approx \sqrt{3} = d_{110}:d_{330} = d_{100}:d_{110}$. With d_3 on the {110} line, one translates the log d strip along the charts of Figures 1 to 6 or on a Hull-Davey chart of the same scale and observes that the pattern can be indexed completely with $c/a = 0.64\,n$ where $n = 1,2,3,\ldots n$. The phase identification is then carried out in the normal manner. Two additional coincidences occur for the combinations $d_4:d_{13}$ and $d_5:d_{16}$. In neither case, however, can the entire pattern be indexed satisfactorily.

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Quantitative Determination of Oxygen in Gases

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Because of the extreme requirements in regard to the oxygen content of the inert gas blankets required in connection with recent developments in technology of liquid metal coolants, it is necessary to have an accurate and sensitive method applicable to the range below 100 p.p.m. of oxygen. The method described is based on the Winkler manganous hydroxide reaction. The method is absolute with a zero blank. The standard deviation for precision is — 0.77 p.p.m. of oxygen and the sensitivity is 0.5 p.p.m. Relatively small samples can be handled, because the reactions can take place below atmospheric pressure. This fact eliminates the need for a carrier gas, thus removing one of the major sources of error. The apparatus is constructed of readily available laboratory equipment and can be made portable. Six to eight samples can be handled during the working day.

THE necessity of measuring the oxygen concentration below 100 p.p.m. in inert blanket gases has become of increasing importance with the development of liquid metal (sodium, sodium-potassium alloy) coolant technology. The available instrumental methods are not satisfactory in this region because of the lack of sensitivity or reproducibility.

A number of chemical methods have been described; recent methods applicable to the range below 100 p.p.m. are those of Brady (*1*), Winslow and Liebhafsky (*7*), and McArthur (*3*). Brady and Winslow and Liebhafsky require the preparation of an oxygen-free carrier gas, which is difficult in itself, while all three methods require large samples of the test gas either to purge the analytical system or because the method is based on passing a large volume of gas through the apparatus. The previous literature has been adequately reviewed in these papers. While this report was in preparation, a paper by Williams, Blachly, and Miller (*5*) was published but did not contain any data to evaluate the sensitivity, precision, or accuracy.

The qualifications of an ideal method for the determination of oxygen in this region should be as follows:

Absolute. The ideal method should be stoichiometric with a zero blank if possible. Only with this requirement can one be sure that the resulting value is not an artifact of the technique in this low range.

Precise. The reproducibility of the values should be at least ± 1 p.p.m. to provide the control required in some phases of liquid metal work.

Sensitive. The method should detect at least 1 p.p.m. of oxygen.

Simplified. The equipment should be rugged and easily constructed of standard laboratory equipment. The use of oxygen-free carrier gases should be eliminated as a possible source of contamination. The apparatus should be portable, so that samples can be taken directly, thus avoiding possible contamination during an intermediate transfer step.

Rapid. The required time of an analysis should be such that answers will be available in a few hours as a maximum, so as to provide adequate control over the process.

Small Samples. In many situations only small samples are available for analysis, such as sampling dry box atmospheres or other small static systems depending on the maintenance of inert atmospheres.

The method described in this paper possesses most of these requirements. It is absolute with a precision of ±1 p.p.m. of oxygen and a sensitivity of 0.5 p.p.m. It is constructed of readily available laboratory equipment and is portable. The time per sample is of the order of 3 hours, but the samples are overlapped so that six to eight samples can be run during a working day. Only relatively small samples are required, as the reactions can take place below atmospheric pressure. This part eliminates the need for a carrier gas, thus removing one of the major sources of contamination.

METHOD

In trying to meet the objectives listed above, the authors tried many of the described procedures and finally concluded that the classical Winkler manganous hydroxide method (*6*) had the most promise as a sensitive stoichiometric procedure. The fundamental reactions involved are (*4*):

$$4Mn(OH)_2 + O_2 + 2H_2O \longrightarrow 4Mn(OH)_3 \quad (1)$$

$$2Mn(OH)_3 + 2I^- + 6H^+ \longrightarrow 2Mn^{++} + I_2 + 6H_2O \quad (2)$$

$$O_2 \equiv 2I_2 \quad (3)$$

A number of sources of error must be eliminated or controlled to meet the optimum requirements. These are indicated in the following list together with the method of control or elimination used in the present paper.

Dissolved Oxygen in Reagent Solutions. In order to eliminate the use of an "oxygen-free" gas as a purging gas to sweep out the dissolved oxygen, simple vacuum techniques are applied. It is not necessary to resort to elaborate means; a simple mechanical pump suffices for this purpose.

Air Oxidation of Iodide to Iodine. This is a serious source of error in the present application, as the oxidation proceeds at a significant rate even in basic solutions. The effect is minimized by using a 1*M* sodium hydroxide–0.1*M* potassium iodide solution freshly prepared immediately before use.

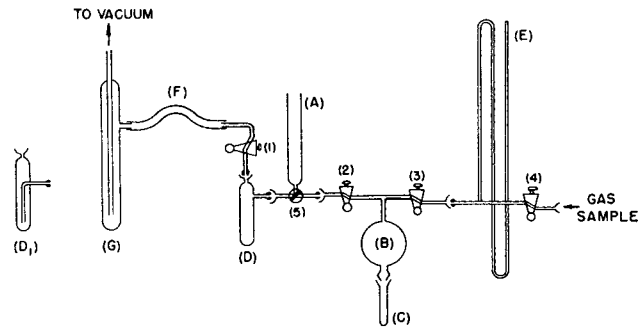


Figure 1. Schematic Drawing of Apparatus

Manganic Ion in Manganous Salt. This is one of the most serious sources of error, since the manganic ion (or ferric ion) in the manganous salt will be determined as oxygen. No source of manganous salt was tried that was satisfactory in this respect. The manganous sulfate used in the determination was prepared by reaction of acid-washed pure electrolytic manganese metal in the dissolver, *A* (Figure 1), with boiled and cooled 0.1*N* sulfuric acid. In the presence of excess metal only manganous ion is formed. A sufficient amount of manganese is dissolved within 15 minutes, which is the time required for the other preliminary manipulations.

Contact between Gas and Solid. One of the drawbacks of the Winkler method is the required reaction between the gas and the precipitated manganous hydroxide. This requirement is the rate-limiting step of the entire process and can be accomplished only by shaking for a long time. The reaction bulb, *B*, was designed to facilitate the contact between the gas and solid as well as to provide a simple means of agitation. This is accomplished by slowly tumbling the flask end over end with the simple appara-

tus shown in Figure 2. As the manganous hydroxide suspension can drain into the side arm, C, each revolution ensures that the walls of the reaction bulb will be freshly coated during each revolution and that the gas will bubble directly through the suspension as it displaces the liquid in the side arm when C is in the vertical position. Under these conditions 2 hours was sufficient for complete reaction between the oxygen and the manganous hydroxide.

Contamination during Acidification. One of the common sources of error is introducing air into the reaction bulb before the basic manganous hydroxide suspension is sufficiently acid. This source of error is eliminated by the simple vacuum technique used.

Determination of Small Amounts of Iodine. The success of the entire method depends on the sensitivity and precision with which the iodine released in the process can be determined. In the earlier days of the investigation, the released iodine was measured volumetrically with thiosulfate, using microweight burets and starch as an indicator. However, more reproducible values were obtained when the iodine was extracted with toluene and measured colorimetrically. The toluene-iodine system is not only stable but has a higher extraction coefficient than the usual solvents like carbon tetrachloride or chloroform.

APPARATUS

The apparatus is shown schematically in Figure 1.

The graduated dissolver cylinder, A, is used for the preparation of the manganous sulfate solution during the preliminary evacuation. The 1-liter reaction bulb, B, is fitted with the side arm, C, attached by a standard-taper joint. This side arm is used for the introduction of the freshly prepared sodium hydroxide–potassium iodide solution. Stopcocks 2 and 3 are the precision vacuum type. They should be spring-loaded or preferably have an evacuated bulb at the end, so they are held in place by atmospheric pressure. This is necessary to prevent loosening of the stopcock barrel during the mixing step. It was found convenient to have the rest of the stopcocks in the apparatus of the same type, but this is not a rigid requirement. The reaction bulb and the other parts of the apparatus are fitted together with semiball joints to enable the disengagement of the various parts during the determination. The pressure tubing, F, is inserted to supply the required flexibility for the same reason.

Trap D is required to catch the first few milliliters of the manganous sulfate before the measured amount of the remainder is transferred to the reaction bulb. The reason for this step is to remove the air entrapped in stopcock 5 bore. Trap D_1 is substituted for D during the acidification step. Cold trap G is a large-volume trap cooled by acetone–dry ice slurry and is used to prevent the carry-over of moisture to the pump. A simple mechanical pump is sufficient, as there is no need to pump below the vapor pressure of water to degas the solution. The closed-end manometer, E, is used to measure the sample pressure, as the system is capable of handling samples of less than atmospheric pressure. This is a valuable attribute of the method, as it allows for the analysis of small samples (less than 1 liter STP) with the same equipment. This aspect of the method enabled the use of very small air samples to prove the accuracy of the procedure.

The use of proper stopcock grease for the components of the reaction flask is important. The grease must be able to withstand the attack of the caustic solutions during the shaking period. Apiezon type N was the only satisfactory lubricant tried. All other types rapidly developed channels, especially at the stopcocks.

PROCEDURE

In order to attain the precision indicated, it is imperative that the reaction bulb be scrupulously clean and the stopcock grease from the preceding determination removed. Excess stopcock grease should not be used, as this often traps some of the released iodine.

Assemble the apparatus as indicated in Figure 1, add 25 ml. of boiled and cooled 0.1M sulfuric acid to the graduated dissolver, A, then add approximately 5 grams of acid-washed pure, electrolytic manganese metal. The reaction will produce manganic-free manganous sulfate as long as an excess of metal is present.

While the manganese sulfate is being prepared, pipet 15 ml. of a freshly prepared solution of 1M sodium hydroxide–0.1M potassium iodide into side arm C and connect to reaction bulb B, using Apiezon-N grease. Evacuate the system to remove the air from the reaction bulb and to degas the caustic-iodide solution. Fifteen minutes of pumping is sufficient for this step.

Close stopcock 1 and run 10 ml. of the manganous sulfate solution into trap D to remove the air trapped in the base of stopcock 5. Then transfer 10 ml. of the manganous solution to the reaction bulb by means of three-way stopcock 5. Manganous hydroxide will be precipitated in the side arm as the acidic solution is neutralized by the sodium hydroxide.

Close stopcock 2, admit the required sample of gas by manipulation of stopcock 4, and record the temperature and pressure. Close stopcocks 3 and 4 and mount the reaction bulb on the mixer which is shown in Figure 2. Tumble the reaction bulb for 2 hours with the speed adjusted so that the side arm will completely fill and empty during each revolution.

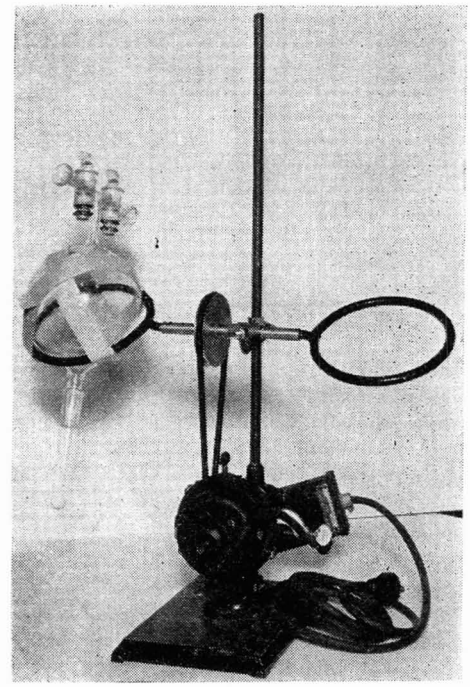


Figure 2. Mixing Device

After the mixing period, replace trap D with trap D_1, which is filled with boiled and cooled 2M sulfuric acid. Reassemble the apparatus, omitting dissolver A and reversing the positions of stopcocks 2 and 3. This step is required, as the semiball joint and glass tubing on this side are still clean and dry. Start the pump and open stopcock 1. When the residual gas is removed from D_1, cautiously open stopcock 3 (now in reversed position) to pump out the gas from the reaction bulb. Besides reducing the pressure in the reaction bulb, this oxygen-free gas passes through the sulfuric acid and removes the last traces of dissolved oxygen. When the pressure in the bulb is low enough, close stopcock 1 and heat trap D_1 with a beaker of hot water which forces the acid over into the reaction bulb.

Close stopcock 3 and remove the reaction bulb from the apparatus. Mix the solutions thoroughly to acidify the contents completely and to dissolve the precipitate. Transfer the aqueous solution to a separatory funnel and extract with toluene. Repeat the extraction to ensure that all the iodine is removed and determine the iodine colorimetrically against a previously established standard curve. For higher oxygen concentrations, titration with thiosulfate to a starch end point is satisfactory.

RESULTS AND DISCUSSION

The blank value for the procedure is essentially zero. The values were obtained by carrying out the determination with no added gas but introducing the manganous solution directly into the evacuated bulb. In a set of nine runs, seven resulted in no detectable iodine (zero blank), while the other two gave the equivalent of 0.9 and 0.3 microliter of oxygen. There was some reason to suspect that these two values were caused by a minute leak. However, including these values, the significance of these deviations was evaluated by using the t-test difference method (*2*). The calculated t value was 1.287, which when compared with the 5% value (2.306) at 8 degrees of freedom indicates no significance to the observed deviations and establishes that the blank value is zero for this determination.

Table I. Recovery of Oxygen from Known Amounts of Air

Oxygen Taken, μl.	Oxygen Found, μl.	Difference μl.	Oxygen Taken, μl.	Oxygen Found, μl.	Difference, μl.
52.3	53.9	+1.6	7.8	10.5	+2.7
52.2	51.5	−0.7	6.3	8.7	+2.4
47.9	44.0	−3.9	1.7	2.3	+0.6
44.7	46.3	+1.6	1.8	2.8	+1.0
41.8	46.8	+5.0	0.7	1.1	+0.4
31.2	26.4	−4.8	0.9	2.0	+1.1
32.9	26.9	−6.0	1.7	1.7	0
29.6	32.5	+2.9	1.8	4.8	+3.0
28.1	26.0	−2.1	1.3	1.5	+0.2
21.0	17.8	−3.2	0	3.6	+3.6
20.0	21.9	+1.9	0	2.0	+2.0
17.5	22.0	+4.5	0	0.7	+0.7
17.0	19.0	+2.0	0	0.8	+0.8
14.7	5.8	−8.9	0	1.2	+1.2
13.7	8.2	−5.5	0	0.9	+0.9
11.6	11.4	−0.2	0	0.7	+0.7
7.1	8.0	+0.9	0	5.7	+5.7
7.8	10.3	+2.5			

Sum of differences for all values = −1.5
Average difference ($\bar{d}$) = 0.0577
$s(d)$ = 3.592
t = 0.0835
$t_{5\%}^{\phi=30}$ = 2.042

In order to evaluate the accuracy of the present method, a large number of recoveries was made using air as the standard. An accurately calibrated 100-ml. gasometer was placed between the reaction bulb and a McLeod gage. The gasometer was fitted with a three-way stopcock, one arm of which was connected to a McLeod gage and the other arm to the reaction bulb.

The standards were prepared by pumping down the gasometer to predetermined pressure as measured by the McLeod gage. Then the stopcock was turned to connect the calibrated volume with the reaction bulb and the gas was pushed into the reaction bulb by displacement with mercury. No helium was added. The rest of the determination was carried out as described above. Thirty-five such determinations were made, varying from an oxygen equivalent of 52 to 0 microliters in order to cover the critical range of application. These data are presented in Table I.

In evaluating the recovery data which are shown in Table I, it is essential to point out that the inherent precision of these data is poorer than the true precision of the method because of the added manipulations and associated errors in measuring and transferring the known air samples. The actual precision of the present method is discussed below.

As there is no blank involved in the method which might indicate a constant analytical bias or cast doubt on the stoichiometry of the method, the proof of absolute accuracy depends on demonstrating that the differences in Table I *do not deviate significantly* from zero. This is most conveniently done by computing the t value for the average algebraic difference, using the method of differences (*2*). The standard deviation, $s(d)$, for the mean difference is 3.592 and the equivalent t value is 0.0835. Since the significant (5%) t value for 30 degrees of freedom is 2.042, it can be stated that the deviation of the differences from zero is completely negligible and therefore the present method is stoichiometric and accurate within the experimental errors involved in the method of preparing the standard samples.

The precision of the method was ascertained by a series of repetitive runs on a tank of relatively pure helium. The oxygen concentration was very low, which affords a test of precision under the most adverse circumstances. The cylinder used was approximately half emptied in the course of the earlier experiments and therefore provided a sample without the layering (nonmixing) effect almost always encountered in high-pressure gas cylinders. If this fact is not recognized, erroneous and discouraging results will be obtained. In a series of seven determinations (0.8 liter STP) an average value of 5.0 p.p.m. was obtained with extreme deviations of +1.0 and −0.8 p.p.m. The standard deviation for precision was 0.77 p.p.m., thus fulfilling the objective of a precision which is at least ±1 p.p.m. of oxygen.

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Infrared Spectra of Metal Isopropoxides

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THE data outlined in this paper originate from a limited investigation into the properties of metal alkoxides. Special interest was devoted to finding absorption bands characteristic of the isopropoxy grouping as it occurs in a variety of molecules. In addition, characteristic absorptions were derived for butoxy, ethoxy, and methoxy groups from spectra available in the literature.

The four spectra determined in this work (Figures 1 to 4) do not appear to be available in the literature and constitute an addition to the small library of spectra of distinctly metallic atoms linked by covalent forces to organic groups.

The present work indicates that absorption bands in the 8.5- to 9.4-micron region consistently appear in the spectra of molecules containing the isopropoxy group, which enables a distinction to be made between this group and most other alkoxy groups.

EXPERIMENTAL WORK

The infrared spectra shown were recorded in the rock-salt region with a Perkin-Elmer Model 21 spectrometer. The sample cell used was approximately 0.12 mm. thick and the compensating cell was approximately 0.11 mm. thick. Carbon tetrachloride and carbon disulfide were employed as solvents. The absorption maxima of the metal isopropoxides are listed in Table I.

MATERIALS

Triisopropyl phosphite (phosphorus triisopropoxide), $P(O_i\text{-}C_3H_7)_3$, was prepared by Thomas Dawson, Chemical and Radio-

The infrared spectra of the triisopropoxides of aluminum, boron, and phosphorus and the tetraisopropoxide of titanium were determined. These spectra were used with spectra in the literature to derive several correlations for isopropoxy and a few other alkoxy groups in the region from 8.5 to 9.4 microns. Characteristic absorptions were found to occur for *n*-butoxy groups at 8.7 (1150 cm.$^{-1}$), 8.9 (1125 cm.$^{-1}$), and 9.3 microns (1075 cm.$^{-1}$); for isopropoxy groups at 8.5 (1175 cm.$^{-1}$), 8.8 (1135 cm.$^{-1}$), and 9.0 microns (1110 cm.$^{-1}$); for ethoxy groups at 8.6 (1160 cm.$^{-1}$) and 9.1 microns (1100 cm.$^{-1}$); and for methoxy groups at 8.4 microns (1190 cm.$^{-1}$).

logical Laboratories, Army Chemical Center, Md. The compound was made as described in the literature (*5*) and purified by treatment with sodium, followed by distillation.

Boron triisopropoxide and boron tri-*n*-butoxide were prepared by Kenneth Mecklenborg, Chemical and Radiological Laboratories, Army Chemical Center, Md. Boron triisopropoxide boiled at 139° at atmospheric pressure, n^{25}_D 1.3770. The boron tri-*n*-butoxide boiled at 88–89° at 3 mm., n^{25}_D 1.4090.

Aluminum triisopropoxide, $Al(O_iC_3H_7)_3$, prepared in the laboratory of the Harshaw Chemical Co., Cleveland, Ohio, was used as received.

Titanium tetraisopropoxide, $Ti(O_iC_3H_7)_4$, supplied by R. I. Bashford, Experimental Station, E. I. du Pont de Nemours & Co., Wilmington, Del., was used as received. Analysis: Ti, 16.3%; calculated for $Ti(O_iC_3H_7)_4$, Ti, 16.9%.

DISCUSSION

Although the metal isopropoxides studied differ widely in weight and electronegativity of the central atom, as well as in the geometry of the molecule, there are bands in the 8.5- to 9.4-micron region that appear to be characteristic of the isopropoxy group.

Tables II to V list the wave lengths of absorption bands in the 8.5- to 9.4-micron region for a variety of molecules containing isopropyl, isopropoxy, and related alkyl and alkoxy groups. Bands are labeled as strong (s), medium (m), weak (w), and shoulder (sh) relative to other intensities in the individual spectra.

It can be seen from an inspection of Tables II and III that characteristic absorptions for isopropoxy occur at or very close to 8.5, 8.8, and 9.0 microns, whereas those for butoxy occur at 8.7 (usually weak), 8.9, and 9.3 microns.

In the case of the isopropoxy absorption bands the 8.5-micron band has been identified as characteristic of iso branching (*7*, *10*). The 8.8-micron band is thought to be an alkyl absorption induced by the proximity of the oxygen atom. The intensity of the 9.0-micron band suggests that it is essentially an oxygen-to-carbon stretching absorption (*11*).

Of the absorption bands that seem to characterize the *n*-butoxy linkage, the weak, sharp 8.7-micron band is probably a normal paraffinic absorption (*7*, *10*). The weak, sharp 8.9-micron band appears to be an induced alkyl absorption, and the broad, strong 9.4-micron band is attributed to oxygen to carbon stretching (*11*). The weak absorptions at 9.32 and 9.37 microns in *n*-pentane (*10*) are undoubtedly normal paraffinic absorptions which are obscured in the alkoxy-containing molecules by the stronger oxygen-to-carbon absorption that occurs at the same position.

Although sufficient data are at present lacking to establish with certainty the position of characteristic absorption for the methoxy and ethoxy groups in the 8.5- to 9.4-micron range, tentative correlations for these groups are: methoxy, a weak, sharp absorption band at 8.4 microns; ethoxy, medium, sharp bands at 8.6 and 9.1 microns (see Tables IV and V). The weakness of the bands in the case of the methoxy and ethoxy groupings suggests that they are not directly associated with the oxygen-to-carbon linkage. The carbon-oxygen bands in methanol and ethanol are at 9.7 and 9.5 microns respectively (*11*), at somewhat longer wave lengths than have been considered here.

The four spectra shown (Figures 1 to 4) all demonstrate a slight hydroxyl absorption in the 2.8- to 3.2-micron region. This is due to a very small amount of hydrolysis, as all these compounds are hygroscopic and subject to hydrolysis. A second common feature is the split 7.25-micron band, characteristic of two terminal methyl groups on a single carbon atom. In the case of the boron triisopropoxide, this terminal methyl splitting absorption is somewhat obscured by strong absorption throughout the 7.0- to 7.5-micron region.

This same strong absorption occurs at 7.0 to 7.5 microns in the spectrum of all molecules with the boron-to-oxygen linkage that have been investigated by the authors and is probably due to a boron-to-oxygen stretching vibration. This bond absorption occurs at a lower wave length than that for phosphorus to oxygen (*4*), probably because of the lower mass of the boron atom.

It is not certain that the band at 7.95 microns marked "Impurity" in Figure 3 is due solely to the presence of a small amount

Table I. Absorption Maxima of Metal Isopropoxides

Aluminum Triisopropoxide	Boron Triisopropoxide	Phosphorus Triisopropoxide	Titanium Triisopropoxide
3.39 (s)	3.38 (s)	3.36 (s)	3.38 (m)
3.43 (sh)	3.43 (m)	3.41 (m)	3.42 (m)
3.52 (m)	3.50 (sh)	3.46 (sh)	3.50 (m)
3.82 (w)	...	...	...
6.83 (m)	6.80 (m)	6.80 (m)	6.84 (m)
...	...	6.86 (m)	6.89 (sh)
...	7.03 (s)	...	7.02 (m)
...	Ca. 7.16 (sh)	...	...
7.20 (m)	7.20 (s)	7.21 (s)	7.19 (m)
7.28 (m)	7.26 (s)	7.27 (s)	7.24 (s)
7.35 (m)	...	7.39 (m)	7.30 (sh)
Ca. 7.40 (sh)	Ca. 7.50 (sh)	...	7.53 (s)
7.50 (w)	...	...	...
...	7.55 (s)	...	...
Ca. 8.03 (sh)	Ca. 7.96 (sh)	7.95 (m)	8.01 (w)
8.29 (m)	...	...	...
8.48 (sh)	...	...	...
8.55 (s)	8.52 (m)	8.50 (m)	8.63 (m)
8.82 (s)	8.80 (sh)	8.78 (s)	Ca. 8.80 (sh)
8.92 (s)	8.90 (s)	9.01 (s)	8.90 (s)
9.69 (s)	...	...	...
...	...	10.00 (s)	Ca. 10.00 (s)
10.55 (s)	10.49 (s)	Ca. 10.48 (s)	Ca. 10.48 (s)
...	...	11.36 (m)	...
...	...	Ca. 11.56 (sh)	...
11.64 (m)	...	11.66 (s)	11.74 (s)
11.98 (s)	11.92 (m)	...	...
13.00 (m)	...	12.98 (m)	...
...	...	13.51 (s)	...
...	...	Ca. 13.80 (sh)	...
14.32 (m)	...	...	...
14.80 (s)	Ca. 14.6 (sh)	...	...
...	15.12 (m)	...	...

Table II. Characteristic Absorption of *n*-Butoxy Group

Compound	Absorption in 8.5- to 9.4-Micron Region			Reference
n-Pentane (1-methylbutane)	8.78 (s)	....	....	(*10*
n-Butanol	Negligible	8.99 (m)	9.33 (s)	(*1*)
Di-*n*-butyl ether	.....	8.9 (s)	9.3 (sh)	(*2*)
n-Butyl acetate	8.68 (w)	8.92 (w)	9.36 (s)	(*9*)
Phosphorus tri-*n*-butoxide (tri-*n*-butyl phosphite)	8.7 (w)	8.9 (w)	9.3 (s)	(*4*)
Boron tri-*n*-butoxide	8.74 (w)	8.97 (w)	9.34 (m)	[a]
Di-*n*-butyl hydrogen phosphite	8.7 (w)	8.9 (w)	9.3 (s)	(*4*)

[a] Spectrum determined in this work although not included in figures in this report.

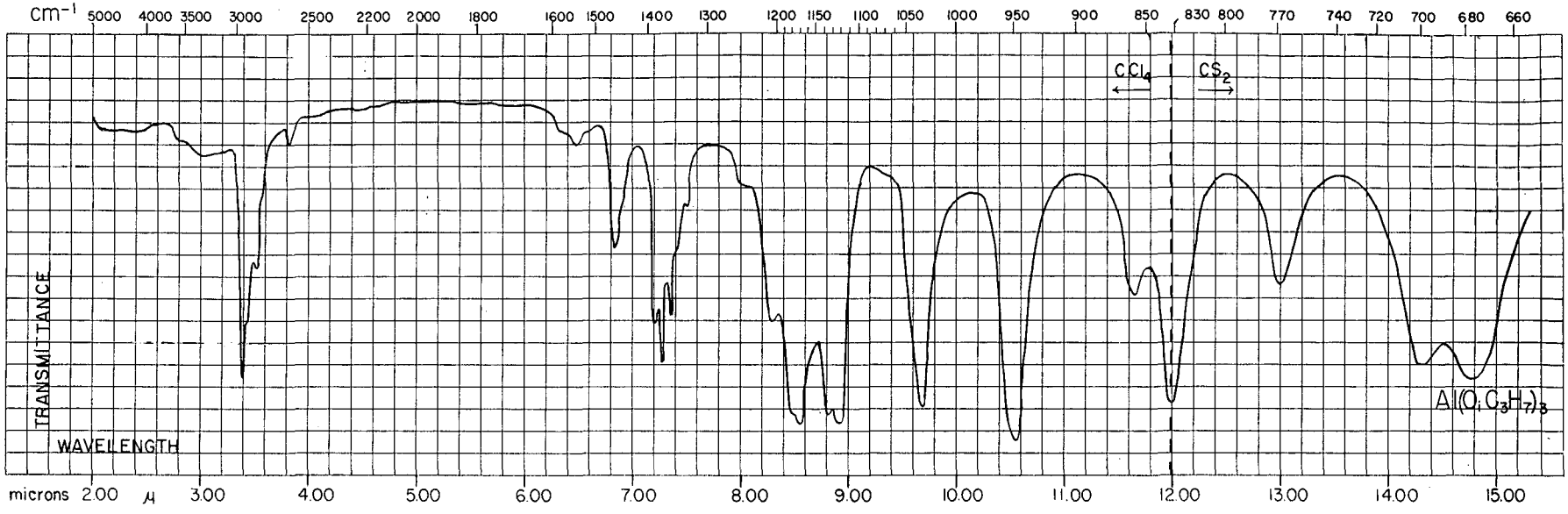


Figure 1. Infrared Spectrum of Aluminum Triisopropoxide

Laboratory purified. Liquid phase. Thickness 0.1 mm. ~8% in CS_2, between 5 and 10% in CCl_4. NaCl prism Resolution S. Pr. 927. Response 1. Gain 6. Speed 4. Suppression 3. Scale 5 cm./micron

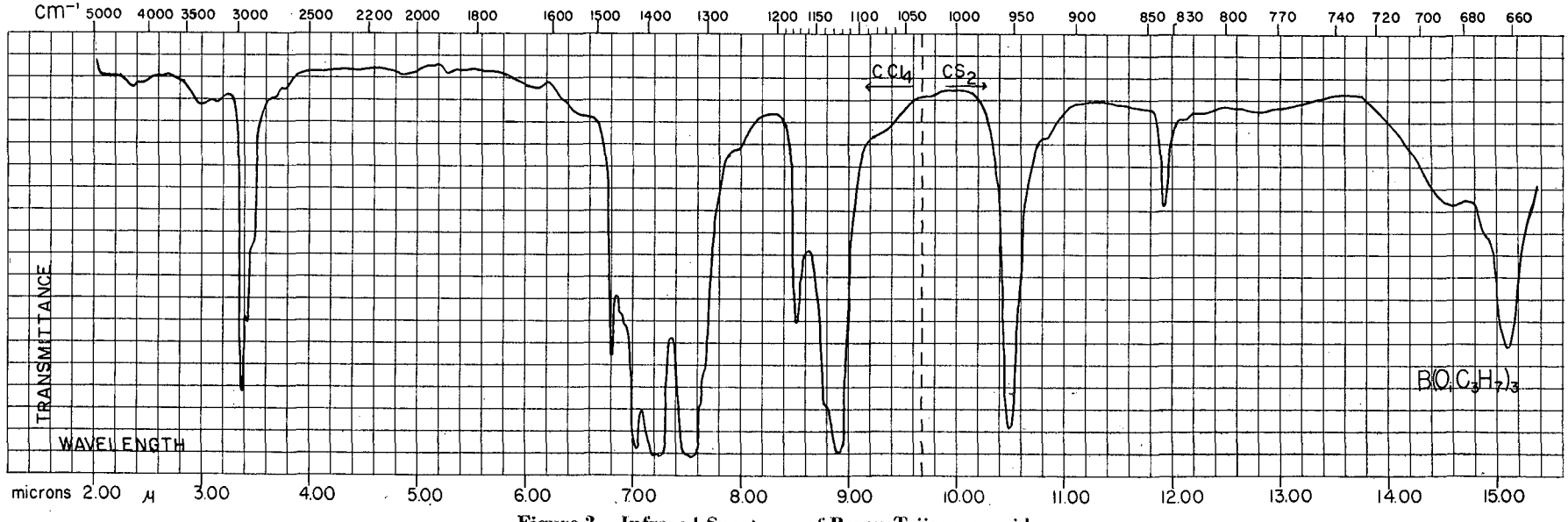


Figure 2. Infrared Spectrum of Boron Triisopropoxide

Laboratory purified. Liquid phase. Thickness 0.1 mm. ~8% in CCl_4, ~8% in CS_2. NaCl prism. Resolution S. Pr. 927. Response 1 Gain 6 Speed 4. Suppression 3. Scale 5 cm./micron

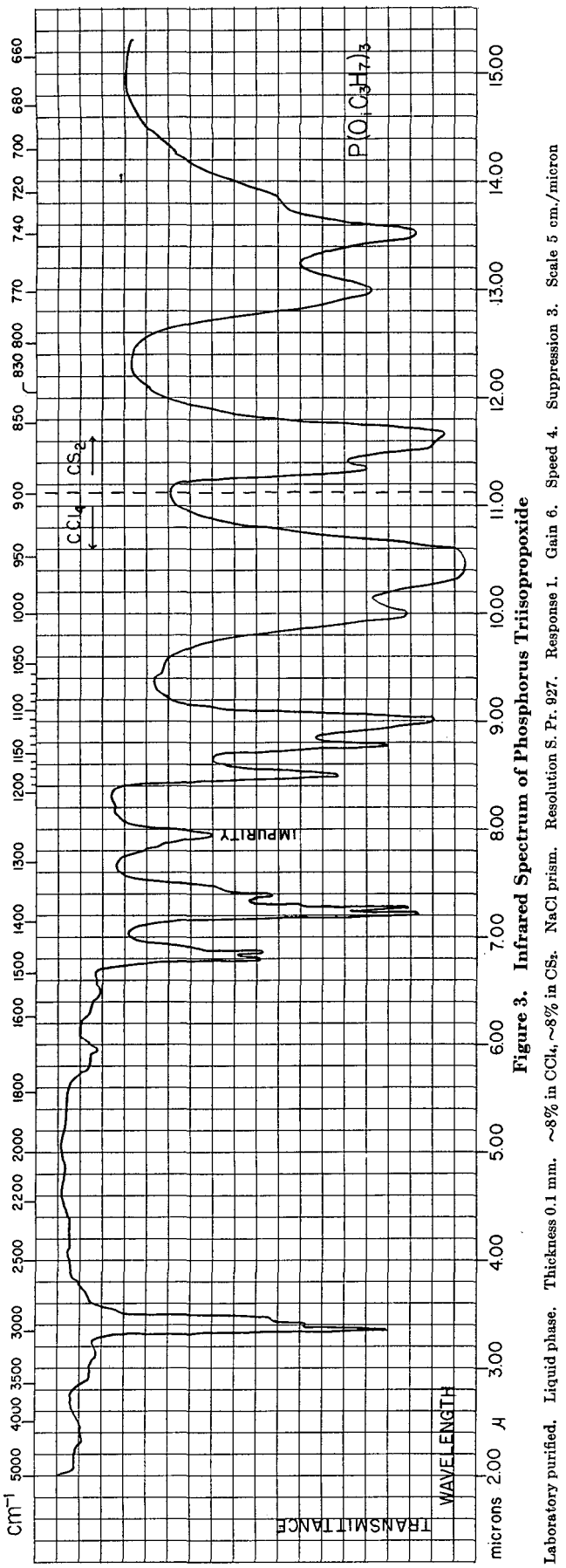


Figure 3. Infrared Spectrum of Phosphorus Triisopropoxide

Laboratory purified. Liquid phase. Thickness 0.1 mm. ~8% in CCl_4, ~8% in CS_2. NaCl prism. Resolution S. Pr. 927. Response 1. Gain 6. Speed 4. Suppression 3. Scale 5 cm./micron

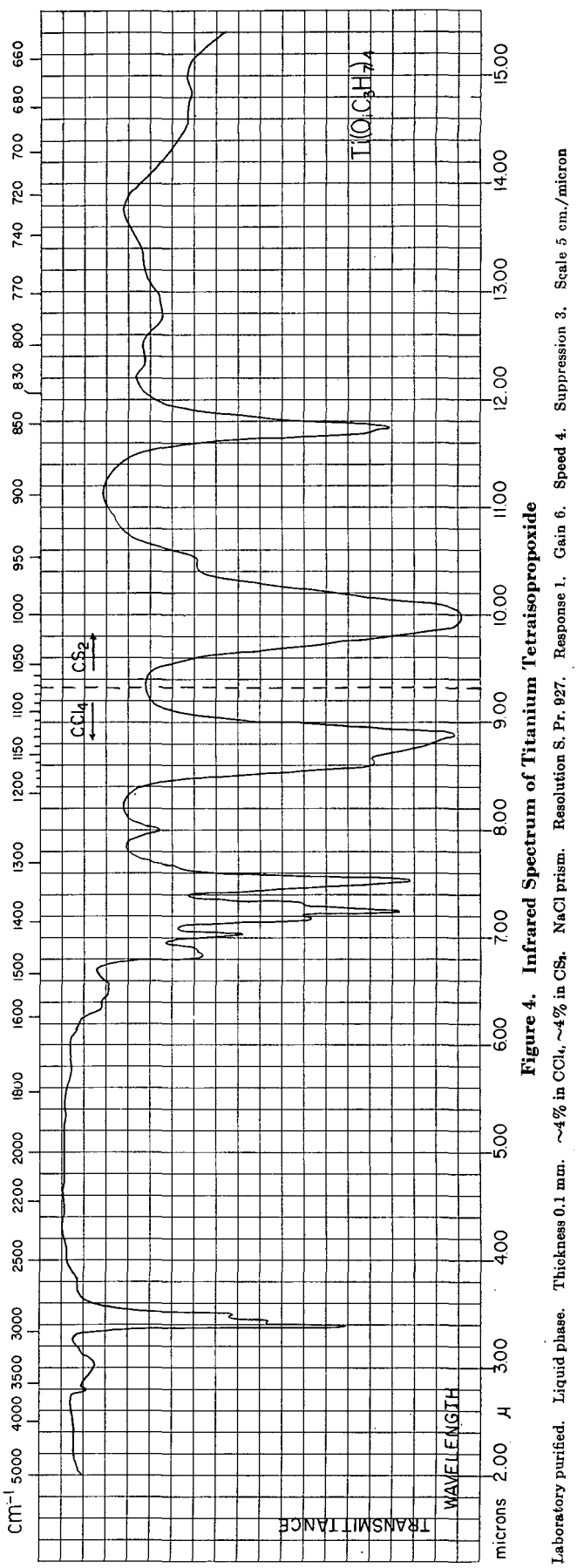


Figure 4. Infrared Spectrum of Titanium Tetraisopropoxide

Laboratory purified. Liquid phase. Thickness 0.1 mm. ~4% in CCl_4, ~4% in CS_2. NaCl prism. Resolution S. Pr. 927. Response 1. Gain 6. Speed 4. Suppression 3. Scale 5 cm./micron

Table III. Characteristic Absorption of Isopropoxy Group

Compound	Absorption in 8.5- to 9.4-Micron Region			Reference
Isobutane (2-methylpropane)	8.50 (s)	....	....	(1)
2-Propanol	8.55 (s)	8.80 (s)	9.00 (sh)	(1)
Diisopropyl ether	8.5 (s)	8.9 (s)	9.00 (s)	(2)
Phosphorus triisopropoxide (triisopropyl phosphite)	8.50 (n)	8.78 (s)	9.01 (s)	Figure 3
Aluminum triisopropoxide	8.55 (s)	8.82 (s)	8.92 (s)	Figure 1
Boron triisopropoxide	8.52 (w)	8.80 (sh)	8.90 (s)	Figure 2
Titanium tetraisopropoxide	8.63 (m)	8.80 (sh)	8.89 s)	Figure 4
Diisopropyl methylphosphonate	8.47 (m)	8.73 (m)	8.99 (m)	(8)
Diisoamyl ether	8.54 (s)	8.84 (s)	9.00 (s)	(9)

Table IV. Characteristic Absorption of Ethoxy Group

Compound	Absorption in 8.5- to 9.4-Micron Region		Reference
n-Propane	8.57 (m)	....	(1)
Ethanol	8.7 (sh)	9.16 (m)	(1)
Diethyl ether	8.8 (s)	9.2 (s)	(2)
Ethyl acetate	8.60 (m)	9.10 (s)	(9)
Phosphorus triethoxide (triethyl phosphite)	8.60 (m)	9.12 (m)	(8)
Triethyl phosphate	8.5 (m)	9.1 (m)	(6)
Diethyl methyl phosphonate	8.59 (m)	9.10 (s)	(8)

Table V. Characteristic Absorption of Methoxy Group

Compound	Absorption in 8.5- to 9.4-Micron Region	Reference
Ethane	....	(1)
Methanol	8.50 (w)	(9)
Dimethyl ether	8.48 (s)	(3)
Methyl carbonate	8.49 (w)	(9)
Phosphorus trimethoxide (trimethyl phosphite)	8.46 (s)	(8)
Dimethyl hydrogen phosphite	8.40 (m)	(8)

of diisopropyl hydrogen phosphite, as an impurity. Diisopropyl hydrogen phosphite, a normal hydrolysis product of phosphorus triisopropoxide (triisopropyl phosphite), has a strong absorption at 7.92 microns due to the P→O linkage (*8*). However, a consideration of the 10.5-micron absorption shown in Figure 3 and the 10.3-micron band in the spectrum of diisopropyl hydrogen phosphite (*8*) suggests that this impurity absorption is probably a normal absorption of phosphorus triisopropoxide strengthened by absorption due to the impurity.

Although most of the bands described appear to be characteristic of the particular alkoxy groups studied, two exceptions have been noted. The spectrum of diisoamyl ether contains bands in the 8.5- to 9.4-micron region nearly identical with bands occurring in molecules containing isopropoxy groups (see Table III). Also, diethyl ether has absorptions at 8.8 and 9.2-microns (see Table IV) which are slightly shifted from the characteristic absorptions (8.6 and 9.1 microns) evidenced in other molecules having ethoxy groups.

The correlations on alkoxy groups derived in this paper are further substantiated by those which have been made between the C—O bond and its absorptions for a large number of alcohols (*11*).

In general, it is felt that the region indicated is a valuable one for characterizing —OR linkages, and that further studies in this region by the method indicated will greatly assist in establishing useful correlations for an otherwise complex portion of the infrared spectrum.

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Colorimetric Determination of Tetrachlorohydroquinone

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DURING an investigation at this laboratory of the use of tetrachlorohydroquinone as a mildew preventive for leather, it was necessary to determine the amount of the fungicide deposited in the leather by the mildewproofing treatment. This amount was expected to range from about 0.2 to about 1.0% of the air-dry leather weight, and should be ascertained to within 0.1% or better. The fungicide can be extracted from the leather with various organic solvents, but tannins, grease, and other leather adjuncts will also be extracted simultaneously. Separation of such mixtures is difficult and should be avoided in developing a useful method.

Among available methods based on the chlorine content, one employing the Stepanov reaction for the ionization of the chlorine (*3*) seemed suitable. However, when applied to alcoholic extractions of the leather, this method failed to give the required accuracy, probably because of the interference of grease and/or tannins. Such methods based on the chlorine content are also of only limited usefulness in this case because of lack of specificity.

A colorimetric method for the determination of chloranil (*2*), the quinone form of tetrachlorohydroquinone, is based on a yellow reaction product of chloranil and diethylamine in acetone. As tetrachlorohydroquinone may be expected to be easily oxidized to chloranil, attempts were made to utilize this method. Anhydrous conditions are required in order to obtain a stable color. The oxidation was therefore made with an organic peroxide dissolved in acetone. Either lauroyl peroxide or benzoyl peroxide apparently readily performed the desired oxidation when applied to solutions of tetrachlorohydroquinone alone. But with acetone extracts of leather, the method failed because the yellow color of the tannins and grease present obscured the color produced by the fungicide. Ethyl acetate extracts less of the tannins and use of this solvent improved the results, but the method still was unsatisfactory, especially for vegetable-tanned leathers.

Chloranil dissolved in epichlorohydrin gives characteristic colors with primary, secondary, and tertiary amines (*4*). A number of amines other than diethylamine were tested with dilute

An investigation of tetrachlorohydroquinone as a leather fungicide required an analytical method for its determination in the presence of grease, tannins, and other leather adjuncts. For this purpose a simple colorimetric procedure has been developed based on a green-blue color produced when the fungicide is added to a benzoyl peroxide–triethylamine mixture, with ethyl acetate as the solvent. The reaction product, which has not been identified, has an absorption band in the visible region of the spectrum with a maximum absorption at 610 mμ. Beer's law is obeyed throughout the working range (0.05 to 0.3 mg. per 50 ml.). Chloranil also gives the color. The recovery of known amounts of tetrachlorohydroquinone in leathers indicates that the method is characterized by a standard deviation of 0.7 mg., or 0.03% based on leather weight when 2.5-gram samples are used. The method should be useful for determining tetrachlorohydroquinone or chloranil in mixtures similar to leather extracts.

solutions of tetrachlorohydroquinone in ethyl acetate containing benzoyl peroxide. Trimethylamine produced a purple, and triethylamine produced a wine-red color under these conditions. All other amines tested produced less suitable yellow or orange colors. As trimethylamine is difficult to handle because of its volatility, further experiments were made with triethylamine. A method based on the wine-red color was developed which gave satisfactory results when applied to leather extracts that contained little or no tannins. With extracts of vegetable-tanned leathers, however, the results were too high because the yellow color of the tannins augmented the photometric measurement of the wine-red color of the fungicide. A reagent blank correction was also necessary.

During this work it was discovered that when the order of addition of reagents is altered so that the extract containing the tetrachlorohydroquinone is added to an ethyl acetate solution of benzoyl peroxide and triethylamine that has been standing for 20 to 30 minutes, the color obtained is green-blue. The color of the green-blue component can be measured without interference from other red or yellow components in the leather extracts because the absorption of light occurs at higher wave lengths. A very simple method for the determination of tetrachlorohydroquinone in leather has been developed based on the green-blue color.

The color is markedly affected by the solvent. Approximately the same result is obtained in benzene and toluene as with ethyl acetate, except that the color development is slower. In ethyl alcohol and acetone the colors are yellow and yellow-green and are not changed appreciably by a change in order of addition of reagents. In chloroform the color is purple-red when triethylamine is added last and orange-red when the sample solution is added to the benzoyl peroxide–triethylamine mixture after 30 minutes. From these observations, and also because it is an excellent solvent for the fungicide extraction, ethyl acetate seems preferable and was used throughout this work.

EQUIPMENT

A Cary Model 12 recording spectrophotometer (20-mm. cell length) was used for the absorption spectra. All other photometric measurements were made with an AC Model Fisher electrophotometer using the logarithmic scale (scale A) and cylindrical 23-ml. cells.

REAGENTS

Ethyl acetate, anhydrous or 80 to 90%.

Benzoyl peroxide, Eastman White Label No. 713. Dissolve 2 grams of benzoyl peroxide in 100 ml. of ethyl acetate and filter through No. 42 Whatman filter paper. This solution should be prepared the same day that it is used.

Triethylamine, Eastman White Label No. 616.

Tetrachlorohydroquinone, Eastman White Label No. 2280.

No special purification of any of the reagents is necessary.

ABSORPTION SPECTRA

The difference in absorption characteristics of the colored solutions produced by changing the order of addition of reagents is shown by Figure 1 (curves 1 and 2). The concentrations of the reagents were identical in the two solutions: 0.25 mg. of tetrachlorohydroquinone, 5 ml. of benzoyl peroxide solution, and 2 ml. of triethylamine, with ethyl acetate as the solvent. The wine-red solution (curve 1) obtained when triethylamine was added to a solution containing tetrachlorohydroquinone and benzoyl peroxide had a maximum absorption in the visible at 530 mμ. The green-blue solution (curve 2) obtained when tetrachlorohydroquinone was added to a benzoyl peroxide–triethylamine solution that had been standing for 30 minutes, had a maximum absorption in the visible at 610 mμ. When chloranil was used instead of tetrachlorohydroquinone, practically identical spectra were obtained, indicating that the same two reaction products were involved. Evidently benzoyl peroxide oxidizes the tetrachlorohydroquinone to chloranil, but it also seems to perform some other function. Without benzoyl peroxide, solutions of chloranil and triethylamine as dilute as those given above give only a slight yellow-green color. A similar yellow color was produced when *tert*-butyl peroxide or lauroyl peroxide was substituted for benzoyl peroxide.

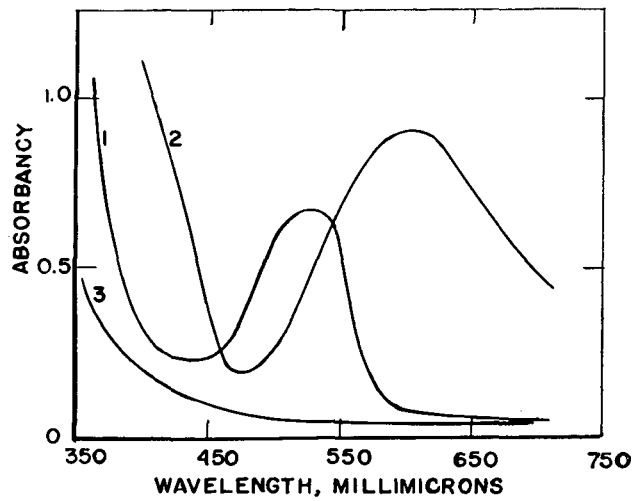


Figure 1. Absorption Spectra

1. Wine-red color. 50 ml. of ethyl acetate solution containing 0.25 mg. of tetrachlorohydroquinone, 100 mg. of benzoyl peroxide, and 2 ml. of triethylamine. Order of adding reagents. Tetrachlorohydroquinone, benzoyl peroxide, triethylamine
2. Green-blue color. Same concentration and reagents as in 1. Order of adding reagents. Tetrachlorohydroquinone added to solution of benzoyl peroxide and triethylamine that has been standing for 30 minutes
3. Blank. Same as 2, but 5-ml. aliquot of 100-ml. ethyl acetate extract of 2.5 grams of a vegetable-tanned leather containing no fungicide added in place of tetrachlorohydroquinone

From Figure 1 (curves 1 and 2) it appears that the reaction products are different for the two alternate orders of reagent addition. Neither of these products has been identified. Figure 1 (curve 3) shows the absorption spectrum of the reaction product obtained with an ethyl acetate extract of a leather containing no fungicide under the conditions which give the green-blue color when tetrachlorohydroquinone is present. It is evident that curve 3 indicates no absorption that will interfere with the measurement of the green-blue color.

Figure 2 shows the calibration curves obtained with the wine-red color and the green-blue color. It is obvious that the latter is

more satisfactory for colorimetric measurements. The procedure given below pertains to the green-blue color only and gives the optimum conditions as determined by a study of all the variables involved when the method is applied to the determination of tetrachlorohydroquinone in leather.

PROCEDURE

Pipet 5 ml. of the benzoyl peroxide solution and 2 ml. of triethylamine into a 50-ml. volumetric flask. Let this mixture stand at room temperature for 30 minutes. Add an aliquot (1 to 5 ml.) of an ethyl acetate solution of the sample containing not over 0.3 mg. of the fungicide, and let the flask stand protected from sunlight at room temperature for 1.5 hours. Dilute to the mark with ethyl acetate and read the color within 30 minutes with ethyl acetate in the reference cell and using a filter with maximum transmittance at about 610 mμ. (A 650-mμ filter was used in the work reported here.) For calibration standards, use 1, 2, 3, 4, 5, and 6 ml. of a solution of tetrachlorohydroquinone in ethyl acetate containing 0.05 mg. of tetrachlorohydroquinone per ml. Treat standards and unknowns exactly alike. (It is best to run unknowns and standards simultaneously.) Read the concentration of tetrachlorohydroquinone in unknown from the constructed calibration curve, or use a calibration factor.

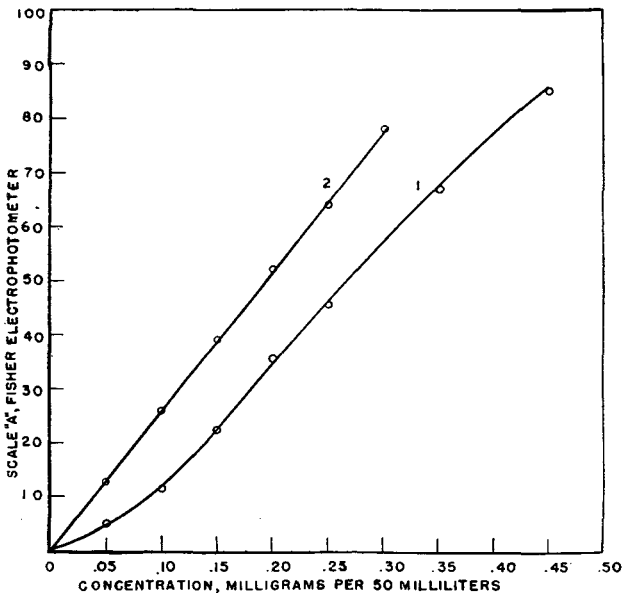


Figure 2. Calibration Curves for Tetrachlorohydroquinone

1. Wine-red color, 525-mμ filter
2. Green-blue color, 650-mμ filter

Table I. Effect of Time Interval

Time Interval, Min.	Photometer Readings[a] 0.10-Mg. standard	0.10-Mg. standard + leather extract
Interval between mixing of benzoyl peroxide and triethylamine and addition of sample		
10	22.5	20.5
15	24.0	22.5
30	25.5	25.0
60	27.5	27.0
Interval between addition of sample and dilution		
Hours		
0.5	18.0	14.5
1.0	23.0	21.0
1.5	25.5	25.0
2.0	24.5	24.0
3.0	22.0	22.0
Interval between dilution and color measurement (color stability)		
Min.		
5	25.0	24.5
10	26.0	24.5
20	25.5	25.0
30	25.5	24.5
60	24.5	23.5
120	22.0	21.5
180	20.5	20.5

[a] Scale A, Fisher electrophotometer, 650-mμ filter.

EFFECT OF CHANGES IN EXPERIMENTAL CONDITIONS

Except for the variable concerned, the procedure given was followed in each of the studies reported in Tables I to III. The photometric measurements are given in the units read directly on scale A of the Fisher electrophotometer using the 650-mμ filter. Observations were made on solutions prepared as the 0.10-mg. standard with and without 1 ml. of a 100-ml. ethyl acetate extract of 2.5 grams of a vegetable-tanned leather.

DETERMINATION OF TETRACHLOROHYDROQUINONE IN LEATHER

Extraction of Fungicide. Extract 2.5 grams of the ground leather in a Soxhlet-type apparatus with ethyl acetate as the solvent. [An ASTM apparatus (*1*) modified for extraction of grease in leather (*6*) was used in this work.] About 15 fillings of the extraction thimble are sufficient. Transfer the extract to a 100-ml. volumetric flask and make to volume with ethyl acetate. Use a 1-ml. aliquot for color development. This dilution is suitable when the amount of the fungicide in the leather does not exceed 1.2%. If higher, further dilution of the extract is necessary. The milligrams tetrachlorohydroquinone found in the

Table II. Effect of Amount of Benzoyl Peroxide Solution

Benzoyl Peroxide Solution, Ml.	Photometer Readings[a] 0.10-Mg. standard	0.10-Mg. standard + leather extract
1	6.0	6.5
2	16.0	20.5
3	23.0	24.5
4	25.5	26.0
5	26.5	26.5
6	27.5	26.5
8	28.5	29.5
10	28.0	31.5

[a] Scale A, Fisher electrophotometer, 650-mμ filter.

Table III. Effect of Amount of Triethylamine

Triethylamine, Ml.	Photometer Readings[a] 0.10-Mg. standard	0.10-Mg. standard + leather extract
1	32.0	29.0
2	26.5	27.0
3	25.0	26.5
4	21.5	22.5
5	17.5	19.5

[a] Scale A, Fisher electrophotometer, 650-mμ filter.

Table IV. Analytical Results

Leather[a] Type	Tannage	Tetrachlorohydroquinone, Mg. Added to leather sample	Found in extract	% Error
Shoe upper	Unknown	25.00	25.20	+0.8
Shoe upper	Chrome, vegetable	25.00	24.80	−0.8
Shoe upper	Chrome only	25.00	25.60	+2.4
Shoe upper	Chrome, Orotan	25.00	25.60	+2.4
Shoe upper	Chrome, Exan	25.00	24.80	−0.8
Shoe upper	Iron, chrome, Monsanto 6254	25.00	25.20	+0.8
Shoe upper	Sulfonyl chloride, Monsanto 6254	5.00	4.88	−2.4
Shoe upper	Sulfonyl chloride, vegetable	10.00	9.75	−2.5
Shoe upper	Sulfonyl chloride, Orotan	15.00	15.38	+2.5
Shoe upper	Chrome, vegetable[b]	20.00	19.50	−2.5
Sole	Vegetable	25.00	24.94	−0.2
Insole	Chrome, vegetable[b]	30.00	28.31	−5.6

[a] (2.5-Gram sample)
[b] Contained about 0.3% paranitrophenol as mildewproofing agent.

color solution times 4 equals per cent tetrachlorohydroquinone in the leather when the sample weight and dilution recommended are used.

Analytical Results, Accuracy, and Precision. Table IV shows the recovery of known amounts of tetrachlorohydroquinone added to 12 different types and tannages of leathers.

The leather samples were placed in the extraction thimbles and measured amounts of a standard solution of tetrachlorohydroquinone in ethyl acetate were added, so that the leather absorbed all of the solution. The thimbles and contents were then placed near a hot plate for evaporation of the solvent, and allowed to stand for several days to ensure any fixation of the fungicide in the leather that might occur. Extraction and determination of the fungicide were then made according to the procedure given.

The results given in Table IV may be used to evaluate the accuracy and precision of the method (*5*). Theoretically, the amounts of tetrachlorohydroquinone found plotted against the amounts added should yield a straight line passing through the origin and having a slope of unity if no bias exists. The actual line obtained, fitted by the method of least squares to the analytical results, had an intercept not significantly different from zero and a slope not significantly different from unity. There is therefore no evidence of bias in the method. The standard deviation of a single measurement calculated from the data is 0.7 mg. This is equivalent to a standard deviation of 0.03% based on the dry leather weight, using the prescribed sample weight (2.5 grams).

DISCUSSION

The color development in solutions containing leather extracts is somewhat slower than with the standards, but the maximum is reached by all solutions when the time intervals given in the procedure are adhered to. Small amounts of water in the sample or in the solvent do not seem to interfere, because practically the same calibration curves have been obtained with 80 to 90% ethyl acetate as with the anhydrous solvent. The color is somewhat sensitive to sunlight. As the benzoyl peroxide solution becomes yellow on standing and may then give erratic results, it should be prepared the same day that it is used.

Under the conditions of the test, quinone and hydroquinone give a faint purple-blue color which is slow in developing, so that these compounds will interfere only if present in considerable amounts.

The method does not distinguish between tetrachlorohydroquinone and chloranil, but for the purpose for which this method was developed this is not important. Both compounds are fungicidal and are probably easily converted from one to the other, depending on the oxidative conditions in the leather.

Phenols and chlorinated phenols do not interfere, nor does any tanning agent or other leather component that has been encountered.

ACKNOWLEDGMENT

This work was supported by funds supplied by the Office of the Quartermaster General, and the author thanks Ray Treichler of the Research and Development Division of that office for his interest and suggestions. The absorption spectra were determined by E. G. Person, Chemistry Division, National Bureau of Standards, and his assistance is gratefully acknowledged.

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Hydrogen Fluoride Solvent System

Apparatus for Polarographic Studies. Rotating Electrode

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The extreme acidity of hydrogen fluoride makes it difficult to construct satisfactory apparatus for precision measurements. Suitable design principles for an apparatus to study liquid hydrogen fluoride solutions conveniently without fear of corrosion or contamination have been attained. The equipment should be fabricated from Kel-F (polytrifluorochloroethylene), thus permitting visual observation and allowing solutions acidic toward hydrogen fluoride to be studied. As an example, a polarographic cell with a rotating microelectrode has been found to operate satisfactorily. An apparatus so designed is versatile and adaptable and should facilitate future studies in the hydrogen fluoride system.

AS A liquid with a high dielectric constant and a very low viscosity, hydrogen fluoride should provide an excellent ionizing solvent. Although the polarographic technique can supply valuable information about reactions in this interesting solvent system, the only previous work reported is that of Clifford and Balog (*2*). One of the principal deterrents to work of this type has been the lack of suitable equipment for handling this corrosive solvent. Consequently, the work of designing and constructing equipment to handle and study liquid hydrogen fluoride solutions was undertaken.

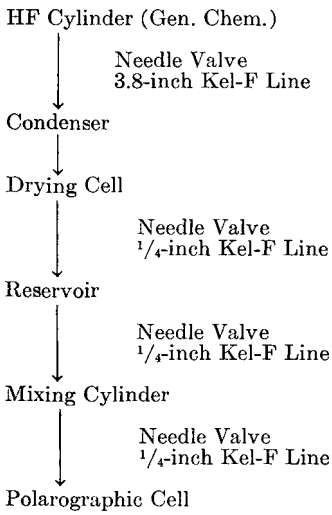
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DESCRIPTION OF EQUIPMENT

Experimental vessels fabricated from a metal such as magnesium are fairly resistant to corrosion by hydrogen fluoride solutions. However, closed vessels must be used, with attendant observational difficulties, and the problem of corrosion reappears when solutions acidic toward hydrogen fluoride (*1*) are used. Fabrication of the equipment from Kel-F, polytrifluorochloro-

ethylene, permits observation and satisfies the need for corrosion-resistant materials to allow handling of solutions acidic toward hydrogen fluoride. In addition the nonwettable character of the Kel-F makes the apparatus easy to clean. The hydrogen fluoride comes in contact with no metal other than the electrodes.

For versatility the apparatus is designed in units which are connected by Kel-F lines, as the following flow chart illustrates.



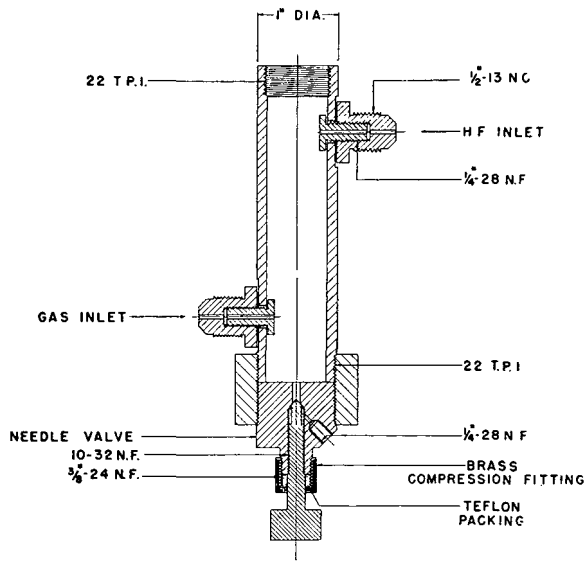


Figure 1. Mixing Cylinder

The condenser is a glass-jacketed length of 3/8-inch Kel-F tubing, connected through a reduction flare fitting of Kel-F to the 1/4-inch inlet line of the drying cell.

As the industrially produced hydrogen fluoride contains small amounts of water and other impurities, it is dried by electrolysis and distilled before use (*3*). The efficiency of the drying operation is attested by the drop in conductivity of the hydrogen fluoride from an initial conductivity of 500 ma. at approximately 7.0 volts to 8 ma. at 12.0 volts (19° C.). The drying cell has a capacity of 50 ml. of liquid hydrogen fluoride. The body of the drying cell was milled from solid 1.5-inch Kel-F rod and equipped with a screw cap. The cap contains five openings: hydrogen fluoride inlet, reflux condenser, leads to the two nickel electrodes, and a vapor outlet. The vapor outlet line (1/4-inch Kel-F tubing) leads through a needle valve to the hydrogen fluoride reservoir.

The reservoir has a capacity of 30 ml. of liquid hydrogen fluoride and is constructed from a length of 1-inch Kel-F tubing with a needle valve at the bottom. The top is closed by a plug with two openings: hydrogen fluoride vapor inlet, and reflux condenser. The reservoir is jacketed with glass for coolant circulation. From the reservoir a 1/4-inch line leads to the mixing cylinder.

Details of the mixing cylinder, also constructed from 1-inch Kel-F tubing, are shown in Figure 1.

The mixing cylinder is equipped with a reflux condenser, a gas inlet (with needle valve) for stirring, and a needle valve at the bottom. All needle valves are similar in principle to the one shown in Figure 1, and are modeled after a standard hoke needle valve. From the mixing cylinder a 1/4-inch line leads to the polarographic cell.

Details of the polarographic cell are shown in Figure 2.

The body of the cell, with a capacity of 25 ml., is milled from solid 1.5-inch Kel-F rod for immersion in a cooling bath. The cell is fitted with a threaded cap with four openings: hydrogen fluoride inlet, reflux outlet, rotating electrode, and electrical connection to the quiet electrode. The aluminum metal rim on the cap retains the mercury which covers the top of the cell during operation.

A mercury pool may be used as the quiet electrode, electrical contact being made through the mercury well shown in Figure 3, or a metal plate with an area many times that of the microelectrode may be inserted.

Details of the rotating electrode are shown in Figure 3.

The metal microelectrode consists of a wire which is press-fitted into the Kel-F shaft through a hole drilled about 0.002 inch smaller than the wire diameter. The wire penetrates into the hollow center of the Kel-F shaft, which is filled with mercury. The mercury in the shaft makes contact with a Nichrome wire which circles the upper rim of the electrode. The entire top of the cell is covered with mercury during operation, the mercury acting as a vapor seal and providing electrical contact with the rotating electrode through the Nichrome wire. The electrode is rotated by a two-phase induction motor, speed variation being obtained by varying the voltage across one phase and keeping the voltage across the other phase constant.

The rotating electrode as shown in Figure 3 is the final design, which was evolved through several stages. The first electrode

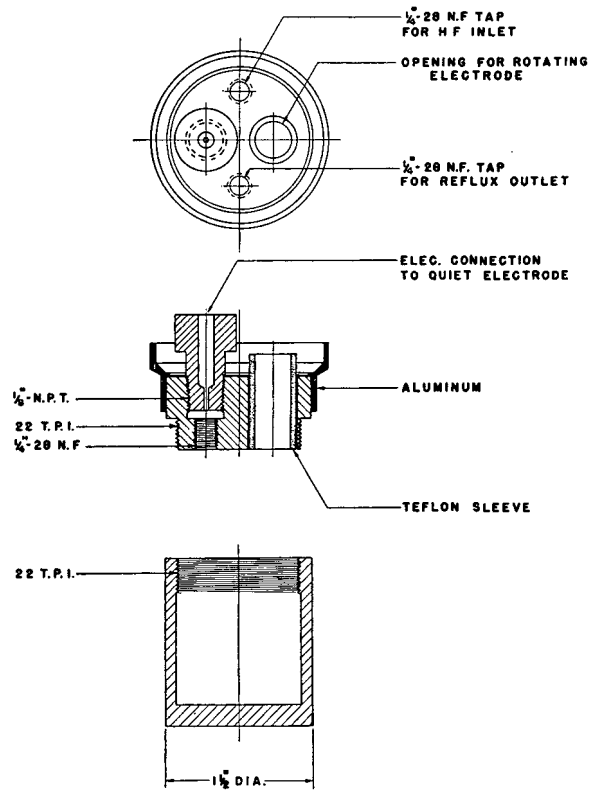


Figure 2. Polarographic Cell

was somewhat smaller and the hole in the cap of the polarographic cell was only slightly larger than the shaft of the electrode. This electrode required precise centering and would not operate for any length of time without binding. The hole through the cell cap was then enlarged somewhat, and a Teflon (polytetrafluoroethylene) sleeve inserted. A similar rotating electrode constructed of Teflon operated fairly satisfactorily. Because Teflon is self-lubricating, any contact of the electrode shaft with the Teflon sleeve did not result in binding. However, Teflon does not have the rigidity of Kel-F and the electrode shaft tended to warp and snap off. Therefore, the electrode was again made of Kel-F and the hole through the cell cap was enlarged to its present size, eliminating the need for precise centering.

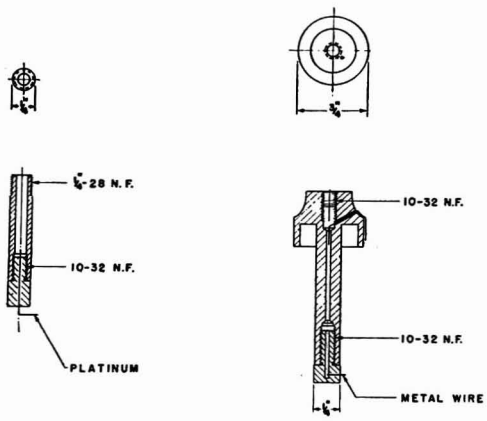


Figure 3. Mercury Well (*Left*) and Rotating Electrode (*Right*)

All condensers and the hydrogen fluoride reservoir are cooled by circulating refrigerated ethyl alcohol (−35° C.). The polarographic cell is cooled by a circulating bath of tetrachloroethylene, kept at 0° ± 0.4° C. The Kel-F lines are joined by flare fittings or threaded joints. The Kel-F tubing can be flared with a standard flaring tool by immersing the tubing and the tool in boiling water to soften the Kel-F. If the tubing is allowed to cool to room temperature before the flaring tool is removed, a permanent flare is obtained. The male fittings are machined from Kel-F (Figure 1), but standard brass flare nuts are used. All fittings and threads are greased with Fluorolube (Hooker). All openings to the atmosphere are protected by indicating Drierite mixed with sodium fluoride pellets.

OPERATION

The apparatus is purged with dry nitrogen, and hydrogen fluoride vapor from the cylinder is condensed into the drying cell. Voltage (12.0 volts) is then applied across the two nickel electrodes and the hydrogen fluoride is electrolyzed until dry. Electrolysis is continued until the conductivity is very low (8 ma. at 12.0 volts). After drying, the hydrogen fluoride is distilled over into the reservoir. The desired amount of liquid hydrogen fluoride is then bled through a needle valve into the mixing cylinder, in which has been placed a weighed amount of organic or other material to be dissolved in the hydrogen fluoride. This solution is stirred thoroughly by bubbling dry nitrogen through the cylinder. After thorough mixing, the solution is let into the polarographic cell through another needle valve. To ensure temperature equilibrium of the hydrogen fluoride solution with the cooling bath, the electrode rotation is started some time before measurements are taken.

The apparatus has been used to study anodic reactions in liquid hydrogen fluoride. The typical current-voltage curve shown in Figure 4 was obtained with a microelectrode of nickel (anode) rotating at 800 r.p.m. The cathode was a nickel plate with an area many times that of the microelectrode. The solution was 0.12*M* barium fluoride in hydrogen fluoride, plus possible trace amounts of water. The potentials measured were applied potentials. The current-voltage curves obtained are time-dependent, but, if the same time interval is used, they are reproducible.

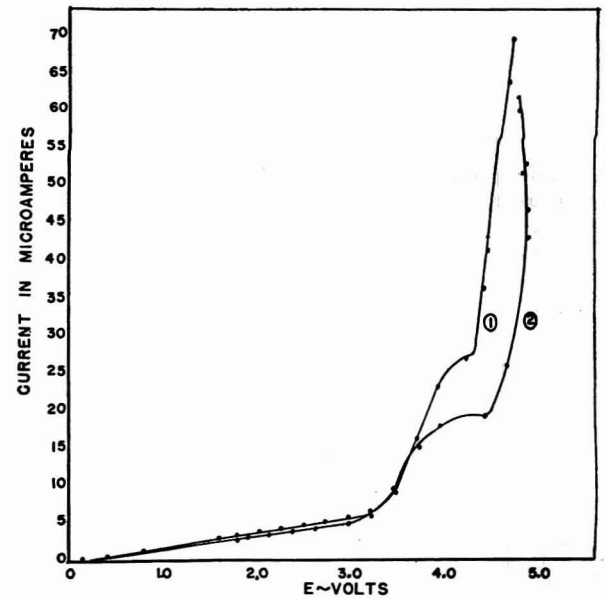


Figure 4. Typical Current-Voltage Curve

1. Decreasing potential
2. Increasing potential

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Identification of Thiophene and Benzene Homologs, Mass Spectral Correlations—Correction

In the article "Identification of Thiophene and Benzene Homologs, Mass Spectral Correlations" [Kenney, I. W., Jr., and Cook, G. L., ANAL. CHEM., **24**, 1391 (1952)], the two paragraphs in the second column on page 1392, beginning "One compound shown . ." and "Rearrangements at the moment . . . . . ," should be omitted. In Table III the pattern shown for *tert*-amylbenzene is erroneous.

The material used to obtain the pattern for *tert*-amylbenzene was a commercial sample redistilled at the Petroleum and Oil-Shale laboratory of the U. S. Bureau of Mines at Laramie, Wyoming. A center cut from this distillation was used to obtain the pattern. It has since become evident that the purchased material was not *tert*-amylbenzene. As a consequence, the special correlations developed for this compound are not necessary, as the corrected pattern fits the general correlations.

Since, publication of the article *tert*-amylbenzene has become available through API Project 6. A corrected pattern for *tert*-amylbenzene based on API standard sample 1014 is shown below:

	%		%
Parent peak	13.8	*m/e* 79	7.5
Parent less 1	...	*m/e* 78	4.5
Parent less 15	2.7	*m/e* 77	9.8
Parent less 29	100.0	*m/e* 43	1.2
Parent less 31	4.3	*m/e* 41	15.3
Parent less 43	3.8		
Parent less 57	54.7		

G. L. COOK

Simple Flexibility Test

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A simple test for flexural rigidity is proposed. Flexural rigidity is not an arbitrary quantity but a standard engineering measure of flexibility. Because of the extreme simplicity of the equipment, technique, and calculation of flexural rigidity, the test may be of value wherever a quantitative measurement of the flexibility of rubber products is needed. An important advantage of this test is that these products may be bent to a degree encountered in service. The test is sensitive to small variations in flexibility. It may be of value in engineering design and development work, and its simplicity would suit it particularly well for control work. Continuous lengths of hose or belting can be tested without being cut. Tests may be conducted at extreme temperatures using an insulated box equipped with hand holes, and used in the laboratory for measuring stock modulus.

FOR some time there has been a need for a simple but meaningful flexibility test for rubber and plastic products. Tests proposed include simple beam and cantilever-type tests and various modifications. Generally these are considered to be small deflection tests.

The flexibility of rubber and plastic products depends on the curvature to which they are bent. If information on the flexibility of belting or hose, for example, is needed for design or development purposes, it should be measured at the desired degree of curvature.

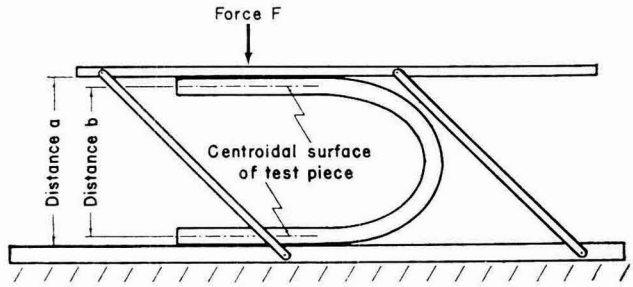


Figure 1. Pantograph Flexibility Tester

The proposed test measures a distance and a force using a simple, inexpensive piece of equipment. A quick calculation yields the flexural rigidity, a standard measure of flexibility in the study of the strength of materials. Although the equipment is simple, the test is sensitive to small variations in flexibility.

DESCRIPTION OF TEST

The test piece, originally straight, is bent into a U-shape in a piece of equipment consisting of two surfaces that are always maintained parallel to each other through a pantograph linkage, as shown in Figure 1. The force, F, and the distance, a, are measured. The distance between centroidal surfaces, b, is calculated, knowing the geometrical shape of the cross section of the test piece. The flexural rigidity, EI, which is the product of modulus of elasticity and moment of inertia of the cross section, can be computed from the formula:

$$EI = 0.34830\ Fb^2$$

If F is measured in pounds and b in inches, the units of EI are (pounds) (inches)^2.

In this test the beam is bent to a radius of curvature of approximately one half b. Actually, the minimum radius is $0.41731b$ at the mid-point of the test piece.

If the test is conducted in a vertical plane and weights are used for force F, the weight of the test piece may introduce a slight error in EI. This error would be least for the most severe bend, or the smallest value of b.

Figures 2 and 3 show the proposed test used on a belt and on hose. Continuous lengths of hose or belting can be tested. As shown in Figure 3, the upper free end of the hose must be held parallel to the upper plane without coming in contact with it.

The degree of bend of the test piece must not be so severe as to alter the shape of the cross section appreciably. Hose, for example, must not be bent to the point where it collapses. In general, rubber products should be bent to the extent encountered in service.

Other types of linkages can be devised for the test equipment. A linkage designed to allow the two parallel surfaces always to move in a direction perpendicular to these surfaces may be considered desirable.

THEORY OF TEST

The test piece is bent into the shape shown in Figure 4 under the colinear forces F, F, until the free ends are parallel. To determine the relationship of flexural rigidity to F and b we start with the well-known equation for the bending moment of a beam:

$$M = EI/r \qquad (1)$$

where EI = flexural rigidity of the beam and r = radius of curvature of the centroidal surface of the beam.

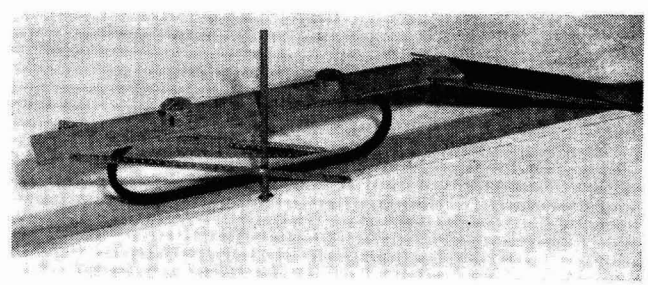


Figure 2. Test of Flexibility of V-Belt

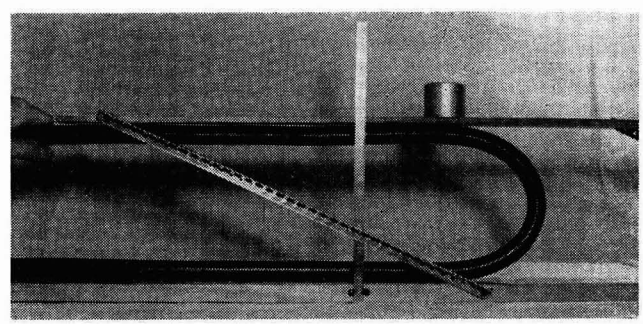


Figure 3. Test of Flexibility of Hose

Now at any point $P(x, y)$ on the centroidal surface $r = -ds/d\theta$ where $\tan\theta$ is the slope at P and s is the distance from O along the surface to P. The minus sign is necessary here, as r is always positive, and $ds/d\theta$ is always negative (as s increases, θ decreases). The moment M at P of forces to the left of P is Fy. Then Equation 1 becomes:

$$-EI\frac{d\theta}{ds} = Fy \tag{2}$$

Differentiating with respect to s and then integrating:

$$\frac{d^2\theta}{ds^2} = -\frac{F}{EI}\times\frac{dy}{ds}$$

$$= -\frac{F}{EI}\sin\theta$$

$$\frac{d\theta}{ds}\times\frac{d^2\theta}{ds^2} = -\frac{F}{EI}\sin\theta\frac{d\theta}{ds}$$

$$\int_0^{d\theta/ds}\frac{d\theta}{ds}\,d\left(\frac{d\theta}{ds}\right) = -\frac{F}{EI}\int_{\pi/2}^{0}\sin\theta\,d\theta$$

$$\frac{1}{2}\left(\frac{d\theta}{ds}\right)^2 = \frac{F}{EI}\cos\theta$$

$$\frac{d\theta}{ds} = -\left(\frac{2F}{EI}\right)^{1/2}\cos^{1/2}\theta$$

The negative root is the correct one here, as $\frac{d\theta}{ds}$ is always negative, and $\left(\frac{2F}{EI}\right)^{1/2}\cos^{1/2}\theta$ is always positive.

Then

$$ds = -\left(\frac{EI}{2F}\right)^{1/2}\frac{d\theta}{\cos^{1/2}\theta} \tag{3}$$

Now to find x_a we must use the relationship:

$$dx = \cos\theta\,ds$$

$$= -\left(\frac{EI}{2F}\right)^{1/2}\cos^{1/2}\theta\,d\theta$$

$$\int_0^{x_a} dx = \left(\frac{EI}{2F}\right)^{1/2}\int_0^{\pi/2}\cos^{1/2}\theta\,d\theta \tag{4}$$

The integral on the right can be obtained by making use of the following relationship (see any good advanced calculus text or table or integrals):

$$\cos^m\theta\,d\theta = \frac{(\pi)^{1/2}}{2}\frac{\Gamma\left(\frac{m+1}{2}\right)}{\Gamma\left(\frac{m}{2}+1\right)}$$

where m has any value > -1 and Γ is the gamma function. When $m = \frac{1}{2}$:

$$\int_0^{\pi/2}\cos^{1/2}\theta\,d\theta = \frac{(\pi)^{1/2}}{2}\frac{\Gamma(3/4)}{\Gamma(1\,1/4)}$$

$$= \frac{(\pi)^{1/2}}{2}\frac{\frac{4}{3}\Gamma(1\,3/4)}{\Gamma(1\,1/4)}$$

$$= \frac{2}{3}(\pi)^{1/2}\frac{0.91906}{0.90640}$$

$$= 1.19814$$

Then Equation 4 becomes:

$$x_a = 1.19814\left(\frac{EI}{2F}\right)^{1/2}$$

Now since $b = 2x_a$, EI can be solved for in terms of b and F:

$$EI = \frac{1}{2(1.19814)^2}Fb^2$$

$$= 0.34830\,Fb^2 \tag{5}$$

This is the relationship we have been seeking.

Certain other quantities may be of interest, such as y_a, s_a, and r_a. y_a can be determined as follows:

$$dy = \sin\theta\,ds$$

$$= -\left(\frac{EI}{2F}\right)^{1/2}\frac{\sin\theta}{\cos^{1/2}\theta}\,d\theta$$

$$\int_0^{y_a} dy = \left(\frac{EI}{2F}\right)^{1/2}\int_0^{\pi/2}\frac{\sin\theta}{\cos^{1/2}\theta}\,d\theta$$

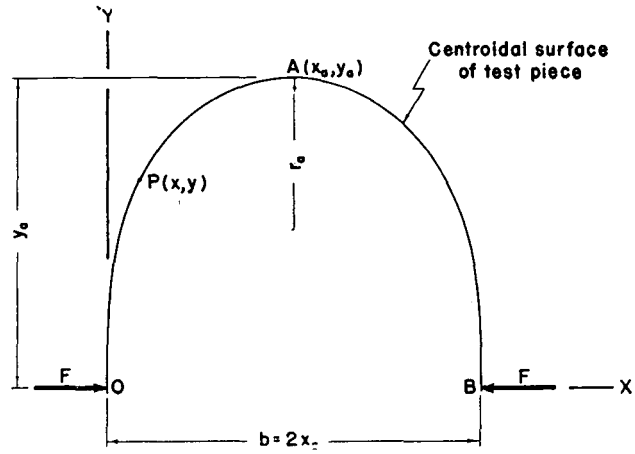


Figure 4. Analysis of Test

The following relationship is known:

$$\int_0^{\pi/2}\sin^m\theta\cos^n\theta\,d\theta = \frac{1}{2}B\left(\frac{m+1}{2},\frac{n+1}{2}\right)$$

$$= \frac{1}{2}\frac{\Gamma\left(\frac{m+1}{2}\right)\Gamma\left(\frac{n+1}{2}\right)}{\Gamma\left(\frac{m+n+2}{2}\right)}$$

where m and $n > -1$ and B is the beta function. If $m = 1$ and $n = -\frac{1}{2}$:

$$\int_0^{\pi/2}\frac{\sin\theta}{\cos^{1/2}\theta}\,d\theta = \frac{1}{2}\frac{\Gamma(1)\Gamma(1/4)}{\Gamma(1\,1/4)}$$

$$= \frac{1}{2}\frac{\Gamma(1)\,4\Gamma(1\,1/4)}{\Gamma(1\,1/4)}$$

$$= 2$$

Then

$$y_a = \left(\frac{2\,EI}{F}\right)^{1/2}$$

But according to Equation 5:

$$\left(\frac{EI}{F}\right)^{1/2} = \frac{1}{\sqrt{2}}\times\frac{b}{1.19814}$$

Then

$$y_a = \frac{b}{1.19814}$$

Or

$$y_a = 0.83463\,b \tag{6}$$

The distance along the beam from O to A, s_a, can be found as follows:

$$\int_0^{s_a} ds = \left(\frac{EI}{2F}\right)^{1/2} \int_0^{\pi/2} \frac{d\theta}{\cos^{1/2}\theta}$$

According to one of the relationships mentioned above:

$$\int_0^{\pi/2} \frac{d\theta}{\cos^{1/2}\theta} = \frac{(\pi)^{1/2}}{2} \frac{\Gamma(1/4)}{\Gamma(3/4)}$$

$$= \frac{(\pi)^{1/2}}{2} \frac{4\,\Gamma(1\,1/4)}{4/3\,\Gamma(1\,3/4)}$$

$$= \frac{3}{2}(\pi)^{1/2} \frac{0.90640}{0.91906}$$

$$= 2.62206$$

Then

$$s_a = 2.62206 \left(\frac{EI}{2F}\right)^{1/2}$$

$$= 2.62206 \frac{b}{2(1.19814)}$$

$$= 1.09422\,b \qquad (7)$$

r_a can be found from Equation 3:

$$r = -\frac{ds}{d\theta} = \left(\frac{EI}{2F}\right)^{1/2} \times \frac{1}{\cos^{1/2}\theta}$$

At O, $\theta = \frac{\pi}{2}$, and $\frac{1}{r} = 0$. As we move along the centroidal surface from O to A, r decreases until it is a minimum at A:

$$r_a = \left(\frac{EI}{2F}\right)^{1/2}$$

$$= \frac{b}{2(1.19814)}$$

$$= 0.41731b \qquad (8)$$

Thus the shape of the centroidal surface is such that in Figure 4

$$r_a = 0.41731b$$
$$y_a = 0.83463b$$
$$OAB \text{ (along beam)} = 2.18844b$$

These dimensions were verified experimentally using the flat spring steel test piece mentioned below.

APPLICATION OF TEST

A test piece of flat spring steel, 0.5 inch wide, 0.0185 inch thick, and about 16 inches long, was tested. The tare weight of the upper plane and connecting arms of the equipment was 1.164 pounds. An analysis of the forces involved shows that the tare weight is equal to the weight of the upper plane plus one half of the sum of the weights of the connecting arms. The distances, a, between the planes were measured for various weights. Now b is the distance between centroidal surfaces. For the rectangular cross section of the spring steel test piece the centroid lies at the middle of the cross section. Then in this case it follows that $b = a - t$, where t is the thickness of the test piece. Weights were applied in 0.441-pound (200-gram) increments. Measurements and computed quantities were as follows:

Weight, Lb.	F, Lb.	a, Inches	b, Inches	EI, Lb. Sq. Inch
0	1.164	4.41	4.39	7.81
0.441	1.605	3.78	3.76	7.90
0.882	2.046	3.36	3.34	7.95
1.323	2.487	3.04	3.02	7.90
1.764	2.928	2.81	2.79	7.94
2.205	3.369	2.60	2.58	7.81

The average EI value is 7.885 pounds sq. inch. The difference in largest and smallest values is $\frac{7.95 - 7.81}{7.81} = 1.8\%$. Thus the flexural rigidity of steel, which, unlike rubber, has a linear stress-strain curve, can be obtained within fairly narrow limits over a range of test conditions.

An upper bound for the error in EI due to the weight of the test piece may be found as follows. The greatest possible error that could be introduced into the value for F is the weight of the spring steel test piece itself, which was 0.041 pound. Then the error in F, as well as in EI, in this experiment was less than 0.041/1.164 = 3.5% for the greatest value of b, and less than 0.041/3.369 = 1.2% for the smallest value of b.

The flexural rigidity of the spring steel test piece was also measured in a cantilever-type test. A series of concentrated loads, P, up to a maximum of 0.077 pound, was applied at a distance L = 6 inches from the supported end. The maximum deflection, d, at the 0.077-pound load, was 0.70 inch. Values of EI were computed according to the formula for a cantilever beam: $EI = (PL^3)/(3d)$. The average for four loadings was found to be 7.936 pounds sq. inch. The difference in average values of flexural rigidity obtained by the pantograph and cantilever methods is $\frac{7.936 - 7.885}{7.885} = 0.6\%$.

The proposed test may also be used for the determination of modulus of elasticity. Thus for the spring steel the moment of inertia, I, of the cross section is:

$$I = wt^3/12$$
$$= (0.5)(0.0185)^3/12$$
$$= 0.26382\,(10^{-6})\text{ inch}^4$$

Since the flexural rigidity, EI, was found to be 7.885 pounds sq. inch, it follows that the modulus of elasticity, E, is:

$$E = \frac{EI}{I}$$

$$= \frac{7.885}{0.26382\,(10^{-6})}$$

$$= 29.89\,(10^6) \text{ pounds sq. inch}$$

An investigation of the flexibility of tubing, of 1/4-inch inside and 1/2-inch outside diameter, made from three types of stock, yielded the following results at 76° F.

Type of Stock	F, Lb.	b, Inches	EI, Lb. Sq. Inch	EI, Average ± Limits of Uncertainty (n = 5, P = 0.95), Lb. Sq. Inch
Neoprene	1.010	2.75	2.66	2.688 ± 0.095
		2.79	2.74	
		2.76	2.68	
		2.71	2.58	
		2.81	2.78	
Rubber	0.570	3.06	1.86	1.786 ± 0.155
		2.94	1.72	
		2.93	1.70	
		2.91	1.68	
		3.15	1.97	
GR-S	0.570	2.40	1.14	1.126 ± 0.021
		2.40	1.14	
		2.38	1.12	
		2.35	1.10	
		2.39	1.13	

Different values for F were used for the three stocks in order to obtain approximately the same degree of bend—that is, values of b. Values in the last column were computed according to the method recommended by the American Society for Testing Materials (*2*).

The limits of uncertainty of average values of EI reflect test error and variations among test pieces. The magnitude of the test error depends largely on the extent to which friction can be minimized in the bearings of the pantograph linkage. For the piece of test equipment used in this investigation, the error due to friction was on the order of ±1% when the connecting arms and the base were at an angle of about 30° or less.

Rubber and rubberlike materials have time-dependent elastic, or viscoelastic, properties. When rubber or plastic products are

tested, it is well always to obtain readings at a given time interval, say 30 seconds, after load application. This was done in the above evaluation of tubing.

The viscoelastic nature of rubbers and plastics is responsible for the nonlinearity of the stress-strain curve. Consequently in a test such as was conducted on the steel spring, where weights were applied in increments, at a certain rate, the flexural rigidity of rubberlike products will not remain constant with increasing degree of bend, but will vary. The amount of variation depends on the material. This would be true in any kind of bend test, however.

A completely satisfactory solution could be obtained by taking the viscoelastic spectrum of the material into consideration. The pertinent theoretical development, taking time or rate into consideration, for cantilever bending has been worked out by Alfrey (*1*). The theoretical development for the proposed test method is beyond the scope of this paper.

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Universal Anticipation of End-Point System for Automatic Titrations

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This work was done to find a means for preventing overtitration in automatic titrations. Overtitration arises principally because of a time lag in the response of the indicator system. The proposed system circumvents this time lag and can be used with almost any indicator system. It consists of withdrawing part of the sample, titrating the remainder at a rapid rate until an end point is reached, then returning the withdrawn portion and titrating at a slow rate to the final end point. Variation in the amount of sample withdrawn, and in the rate of the slow titration, permits adaptation to a specific titration. Such an anticipation system has been designed for an automatic titrator used to titrate microsamples of oxidizing agents. The results of titration of dichromate samples show a standard deviation of less than 1%. The system extends the applicability of automatic titrators by making it possible to use sluggishly responding indicator systems. It also permits faster titrations without danger of overtitration.

ONE of the major problems of automatic titrations is stopping the addition of titrant in time to prevent overshooting the end point. This generally calls for some means of anticipating the end point, either by the behavior of the indicator system itself or by some external system. This problem is discussed in a previous paper (*1*). The need for this anticipation of end point arises because the indicator response is never instantaneous. The response is affected by the rate of stirring of the solution, the rate of addition of the reagent, the type of indicator, and the physical form of the titration vessel with respect to the location of indicator electrodes, reagent addition point, nonuniform mixing of the solution and sluggish, but eventually stoichiometric, reactions. The more sluggish the response of the indicator system, the more necessary is the need of anticipation to obtain accurate results.

In view of the numerous indicator systems that are useful in automatic titrations, a desirable anticipation system should be independent of the indicator system, and should also be independent of the speed of indicator response in the sense that either fast or slow indicator systems can be used. Müller (*3*) has discussed such an anticipation system in his column on instrumentation, but up to this time the writer is unaware of any reported titrator that has actually used the system. The device described in this paper operates essentially in the manner proposed by Müller.

The system consists of withdrawing part of the sample before titration, titrating the remainder at a rapid rate until an end point is obtained, returning the withdrawn portion, and titrating the remaining sample by the addition of small increments of titrant. The first end point is overshot by a small excess of titrant, the amount of solution withdrawn must contain sufficient sample to react with this excess. The remaining sample is titrated with small increments of titrant; sufficient time is allowed between increments to allow the indicator system to come to equilibrium. The titration can then proceed to an end point that is not overshot by more than a nominal excess of titrant. Variation in the amount of withdrawn sample, increment size, and time between addition of increments permits adaptation to any indicator system, no matter how sluggish its behavior.

An automatic titrator using this anticipation system has been tested for the titration of oxidizing agents with electrolytically generated ferrous ion according to the method of Cooke and Furman (*2*). The basic design of the titrator has been given (*1*). The controller circuit is given in Figure 1.

At the start of a titration, all of the relays are in the open position shown in the figure, the trigger relay (not shown) operates when the indicator potential is above the end-point potential (excess oxidant present). Closure of the "operate" switch to the titration position starts the titration. The circuit (via *K*-5) to the anticipation system solenoid is energized, as is the circuit (via *K*-5 and the trigger relay) to the output relays, *K*-2, *K*-3, which control the addition of titration current and the stopwatch. Energizing the solenoid withdraws a portion of the sample solution from the titration zone (see Figure 2). The titration continues until the remaining portion of the sample has been titrated to the stage where the indicator potential decreases below the end-point potential, which opens the trigger relay contacts. The output relays, *K*-2, *K*-3, now open and the addition of titration current is stopped.

Opening *K*-3 closes a duration of end-point timing circuit (the 2050 thyratron and the R-C network *C*-1, *R*-1), which is set for 1 to 2 seconds. When an end point persists for this time, the thyratron fires, and relay *K*-6 closes, which in turn closes *K*-5, which locks in electrically. Closure of *K*-5 activates the increment addition circuit (*K*-7 and the 12AU7 network), and opens the solenoid circuit, permitting the withheld portion of the sample to return to the titration zone. Part of this portion of the sample

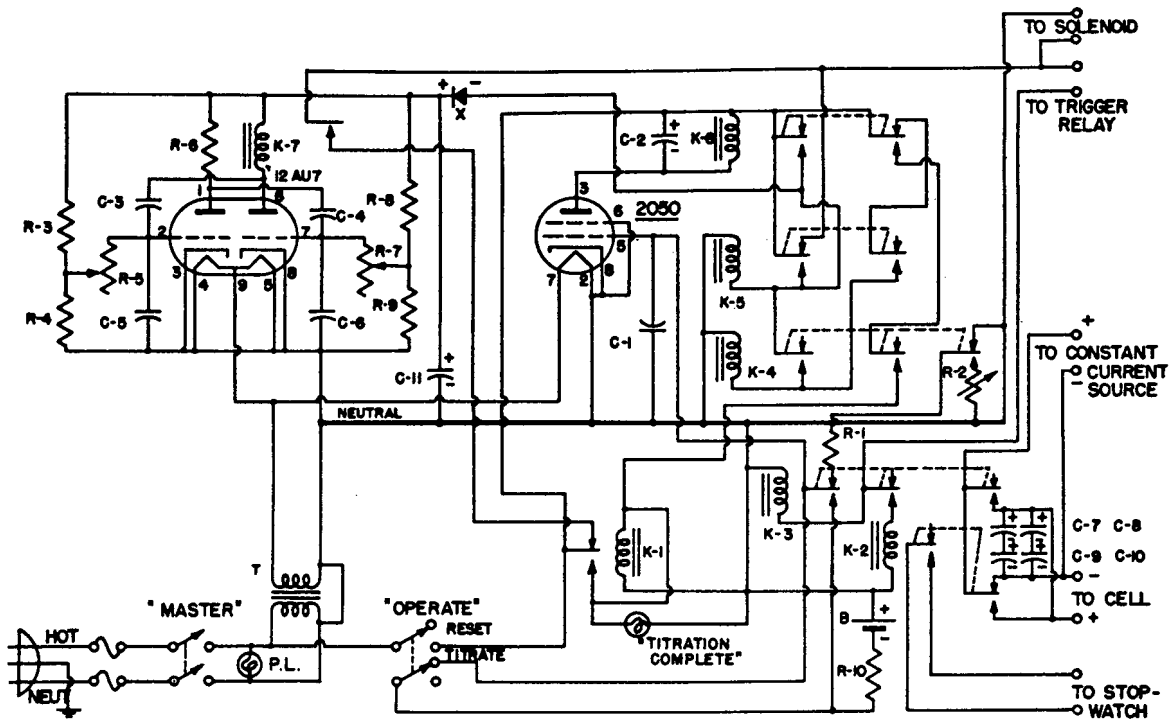


Figure 1. Wiring Diagram of Oxidant Controller

R-1. Resistor, 1 megohm, 0.5 watt
R-2. Resistor, 5-megohm potentiometer
R-3. Resistor, 300,000 ohms, 1 watt
R-4. Resistor, 220,000 ohms, 1 watt
R-5. Resistor, 500,000-ohm potentiometer
R-6. Resistor, 150,000 ohms, 1 watt
R-7. Resistor, 1-megohm potentiometer
R-8. Resistor, 180,000 ohms, 1 watt
R-9. Resistor, 22,000 ohms, 1 watt
R-10. Resistor, 10,000 ohms, 0.5 watt
C-1. Condenser, 1 mfd., 150 volts, dry electrolytic
C-2. Condenser, 4 mfd., 450 volts, dry electrolytic
C-3, *C*-4. Condensers, 4 mfd., 450 volts, dry electrolytic
C-5, *C*-6. Condensers, 0.01 mfd., mica
C-7, *C*-8, *C*-9, *C*-10. Condensers, 20 mfd., 450 volts, dry electrolytic
C-11. Condenser, 40 mfd., 450 volts, dry electrolytic
T. Transformer, filament
B. Battery, 22.5-volt C
P.L. Pilot light
X. Rectifier, selenium, 100 ma.
K-1. Relay, SPDT, 110-volt a.c., coil, Dunco (Struthers-Dunn Co.) 1XAX
K-2. Relay, DPDT, 110-volt a.c., coil, Dunco 1XBX
K-3. Relay, 3PDT, 110-volt a.c., coil, Dunco 1XCX
K-4. Relay, 3PDT, 110-volt a.c., coil, Dunco 1XCX
K-5. Relay, DPDT, 110-volt a.c., coil, Dunco 1XBX
K-6. Relay, DPDT, 5000-ohm d.c., coil, C.P. Clare Type C
K-7. Relay, SPST, 10,000-ohm d.c., coil, Leach 1024-A

reacts with the excess reagent generated in the overtitration, and the remainder raises the indicator potential above the end-point potential, causing the trigger relay to close. However, no titration occurs until the increment addition circuit (*K*-7 and the 12AU7 circuit) operates in the "on" cycle. Both *K*-7 and the trigger must be closed at this stage for titrant to be added. The titration now proceeds by the addition of small increments. The solenoid operates each time an increment is added; this action permits thorough rinsing of the hold chamber to free it from untitrated sample. Titration continues until the indicator potential reaches the second end point.

The first increment addition breaks the end-point timing circuit at *K*-3. This permits *K*-6 to open, which closes *K*-4. Closing *K*-4 inserts resistance *R*-2 into the end-point timing circuit, which permits a delay of up to about 40 seconds; this delay is required to allow for sufficient time between increments. The titration is stopped after the indicator potential decreases to the end-point potential a second time. This opens the trigger circuit, and hence *K*-3 and *K*-2 as before. Opening *K*-3 again closes the end-point timing circuit, now set at 30 to 40 seconds. After this time, *K*-6 again closes, and operates *K*-1, which locks in electrically, and opens the circuit to *K*-7, preventing any spurious titrations after an established end point. Opening the operate switch to "reset" restores the circuit.

The requirements and functions of the trigger output relay circuit, *K*-2 and *K*-3, the duration of end-point circuit (*K*-6, *K*-3, and the 2050 thyratron circuits), and the lockout circuit, *K*-1, have been described (*1*). The function of *K*-4 and *K*-6 is to change the titration from continuous to incremental. Two relays are used to effect the change-over in order to permit the use of one thyratron relay circuit and to prevent false lockouts. The increment addition circuit is a conventional multivibrator circuit, although the frequency of oscillation is lower than is usual in this type of circuit.

A titration assembly is shown in Figure 2. Only the dimensions of the side arm of the titration cell are critical. The design

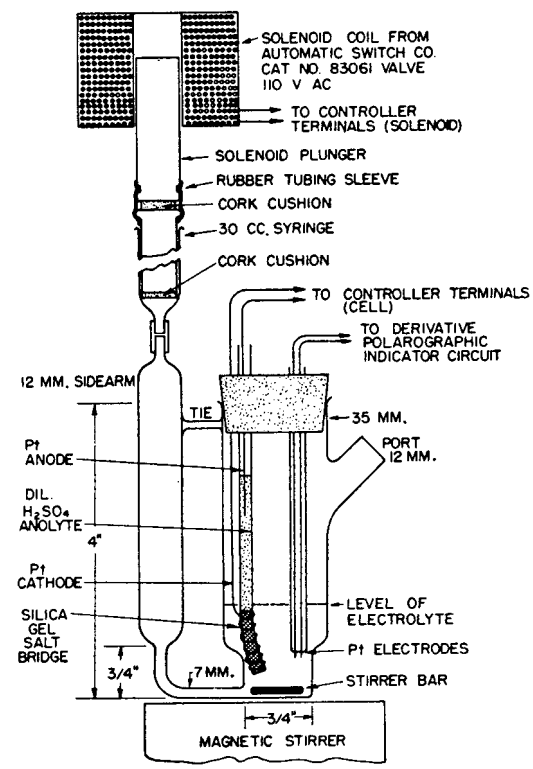


Figure 2. Titration Assembly

Table I. Automatic Titration of Dichromate Standards

N Taken	N Found	Precision, %
0.09810	0.09818	±0.67
0.0500	0.04997	0.48
0.0100	0.01005	0.76
0.00500	0.004943	0.69
0.00100	0.001004	0.74
0.1021	0.1022	0.36

must be essentially as shown in order to prevent pumping of air from the side arm into the vessel in place of the solution. Pumping occurs if a bulb is used in place of the long tube or if capillary tubing is used to connect the side arm. The amount of solution withdrawn is determined by the position of the barrel of the hypodermic syringe in relation to the plunger assembly. From 10 to 20% of the solution should be withdrawn; the rate of stirring, indicator response, titration current, and amount of sample all affect the amount of "overshoot" that must be overcome. A cork or rubber cushion between the solenoid plunger and the syringe plunger is required to prevent breakage; a similar cushion at the end of the syringe plunger is recommended.

Table I gives the results of a set of titrations of dichromate standards using the anticipation system. It was not possible to perform this titration automatically without end-point anticipation, as the indicator lag is large. The derivative polarographic indicator system (*4*) was used. The electrolyte was 4*N* sulfuric acid–0.6*M* ferric ammonium sulfate as prescribed by Cooke (*2*). In the procedure, an unmeasured sample was added to 5 ml. of the electrolyte and titrated to the end point; this pretreated the electrolyte to remove traces of oxidizing or reducing impurity. A series of two to five measured samples (100 µl.) was then run in succession with this treated electrolyte. The dichromate standards were made from triply distilled water and the dried salt. The precision is the standard deviation of a single value, as calculated from 10 results.

The results show that the anticipation system works satisfactorily. The titrator is now being investigated for use in the titration of other oxidizing agents and reducing agents.

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Determination of Polystyrene in Styrenated Alkyd and Styrenated Epoxy Resins

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A quantitative method for determining polystyrene was needed for quality control and acceptance of quick-drying styrene-modified alkyd resins. The styrenated epoxy resins were investigated because of their related modification and their possible future interest to the Ordnance Department. Two procedures for determining the polystyrene have been developed. One is applicable to either the alkyd or epoxy resins. The other, applicable to alkyds only, allows the subsequent determination of the oil acid content of the alkyd resin. Composition requirements of styrenated alkyds can be established and analytical control exercised. The extent to which monomer styrene is converted to polystyrene in the preparation of styrenated resins and oils can be determined.

OF THE synthetic resins, the alkyds probably possess the widest range of applicability, especially for automotive equipment. They are unusually tough and durable and possess excellent solubility, compatibility, adhesion, and gloss retention. Compared to other synthetic resins they are relatively slow-drying. To incorporate the alkyd resins in a quick-drying enamel for ammunition finishing (*2*), they have been modified with styrene. At the present time no analytical control is exercised over the styrene content of these enamels and no composition requirements have been specified, because of the lack of an analytical procedure for determining the styrene. By applying the method of analysis to ten commercially available styrenated alkyds, it has been found that the polystyrene content varies from 26 to 44% of the nonvolatile portion of the solutions. The composition of some of these resins is shown in Table I.

Polystyrene is very resistant to the action of alkalies in alcoholic and nonaqueous media. Because phthalic anhydride in alkyd resins is separated and determined by saponification, styrene, if present, would be found in the filtrate from the phthalic determination. Upon removal of all solvents, the dried products, consisting mostly of excess potassium hydroxide, polystyrene, drying oil soaps, and polyhydric alcohols, can be treated with 87% methanol and the styrene separated, dried, and weighed. The product is insoluble in water but slightly soluble in absolute methanol and in aqueous alkali. However, it separates quantitatively in filterable form from a solution of 87% methanol, even in the presence of excess alkali.

As styrene-modified epoxy resins are of current interest, they were tested by the procedure described. It was found that epoxy resins resist saponification by any medium that can subsequently be evaporated to dryness. By controlled fusion with potassium hydroxide pellets, the epoxy resin could be decomposed and the styrene left unchanged. The same technique can be applied to the styrenated alkyds, but not as conveniently as by the method reported here in detail. Interference of certain unsaponifiable resins can be prevented by using the fusion technique.

ANALYTICAL PROCEDURE

Method for Styrenated Alkyd Resins. To determine the polystyrene in styrenated alkyds, the phthalic anhydride should first

Table I. Composition of Resins

	Nonvolatile, %	Phthalic Anhydride, %	Styrene, %
Commercially Available Styrenated Alkyd Resins			
A	51.0	24.0	34.2
B	62.7	19.1	42.6
C	61.0	24.2	32.8
D	61.6	21.4	35.6
E	50.7	21.9	35.8
F	51.5	21.9	44.4
G	51.0	26.3	35.5
H	60.5	21.8	32.1
I	50.2	22.4	39.0
J	50.9	27.3	26.0
Styrenated Epoxy Resin (Known Styrene Content 33.3%)			
A	50.0		33.8
			33.5
			34.0
			33.6

be removed by the following procedure, which is used to measure the phthalic anhydride gravimetrically. The determination can be conducted without removal of the phthalic anhydride, but it is not recommended, as the presence of dipotassium phthalate retards the drying.

A sample of the isolated vehicle, containing from 0.3 to 0.6 gram of nonvolatile material (1 to 2 grams of vehicle, *3*), is weighed into a 500-ml. Erlenmeyer flask having a 24/40 ground joint; 100 ml. of benzene are added, and the samples swirled or warmed until completely dissolved. Then 50 ml. of 1.0*N* alcoholic potassium hydroxide (66 grams per liter of absolute ethyl alcohol) are added and the sample is refluxed under an air condenser for 1 hour or longer. The condensers are then replaced with loose-fitting corks and the flasks transferred to a 50° C. oven, where they are allowed to cool to the oven temperature for convenient handling. The warm solution is filtered through a dried and weighed fritted-glass crucible of coarse porosity, previously prepared with a mat of asbestos. The precipitate is transferred and washed, first with benzene and finally with absolute ethyl alcohol. If, during the benzene washing, the filtering rate decreases sharply, some ethyl alcohol should be mixed with the wash medium. The filtrate is retained in a clean, dry suction flask. The dipotassium phthalate in the filtering crucible is dried at 100° C. for 1 hour, cooled, and weighed. The usual calculation for phthalic anhydride is used:

$$\% \text{ phthalic anhydride} = \frac{\text{weight of dipotassium salts} \times 61.1}{\text{weight of vehicle} \times \text{vehicle solids}}$$

The filtrate from the phthalic determination is transferred to a 400-ml. beaker, being washed with small portions of benzene. The solvents are evaporated under a hood using an 80° C. glycol bath and a current of air. When the solvent volume has been reduced to approximately 5 ml., 5 ml. of absolute methanol are added, the sample is agitated, and the evaporation is continued to apparent dryness. If the sample contains appreciable quantities of styrene monomer, several repeated evaporations with methanol are necessary. Fifteen milliliters of water are thoroughly mixed with 100 ml. of absolute methanol (or 115 ml. of 87% methanol) and added to the sample. A glass stirring rod is inserted and the beaker is covered and warmed in a bath at 65° C. The sample is stirred every 10 minutes and all portions of the solid matter are loosened from the sides and bottom of the beaker. All lumps or large particles are broken up with the rod.

After 30 minutes, the sample is removed from the bath, cooled to room temperature, then filtered through a dried, weighed fritted-glass crucible of coarse porosity, previously prepared with a mat of asbestos When all of the methanol solution has drained through the crucible, transfer of the sample is continued with water only. When all of the sample has been transferred to the crucible, washing with water is continued until the washings show no alkalinity when tested with indicator paper. The residue is then dried at 110° C., cooled, and weighed. Calculation is made directly on the nonvolatile vehicle:

$$\% \text{ polystyrene} = \frac{\text{weight of residue} \times 100}{\text{weight of vehicle} \times \text{vehicle solids}}$$

Method for Styrenated Epoxy Resins (also suitable for alkyd resins). A sample of the isolated vehicle, containing from 0.3 to 0.6 gram of nonvolatile material, is weighed into a nickel crucible of 30-ml. capacity. Six grams of potassium hydroxide pellets are added and the contents of the crucible are dried in an oven at 110° C. for 3 hours.

An electric heater having a built-in variable transformer instead of a rheostat, such as Precision Scientific Ful Kontrol heater, is used for the fusion of the sample. The heater is fitted with an upper refractory having a 1.25- or 1.5-inch hole, whichever supports the nickel crucible in such manner that the bottom of the crucible does not come in contact with the heating coils. The correct setting or temperature to use must first be established in the following manner. A nickel crucible of the same dimensions as that used for the sample is placed in the upper refractory of the heater and 5 ml. of *n*-butyl phthalate are added. The crucible is provided with a small glass cover and heated at various dial settings for 30 minutes, until the setting is found at which the temperature of the *n*-butyl phthalate is 235° C. when tested with a thermometer. Different heaters require different settings, which must be established in the prescribed manner in order to avoid erroneous results.

The crucible containing the dried sample is covered with a small glass and placed in the refractory of the preheated heater. After 15 minutes, the cover is removed and a short nickel stirring rod, which does not protrude above the rim of the crucible, is inserted. The melt is stirred with the stirring rod for a few seconds, being handled with tweezers. The nickel rod is left in the sample, the crucible covered, and the heating continued. The stirring is repeated every 15 minutes. After 45 minutes' total fusion time, the crucible and rod are transferred to a 400-ml. beaker, the contents are poured out into the bottom of the beaker, 115 ml. of 87% methanol (15 ml. of water plus 100 ml. of absolute methanol) are added, a glass stirring rod is inserted, and the beaker is covered and warmed at the approximate boiling point (65° C. bath) of the mixture until all portions of the sample are loosened from the crucible and beaker and broken into small particles. The mixture is then cooled to room temperature and filtered through a dry fritted-glass crucible of coarse porosity, previously prepared with a mat of asbestos.

When all of the methanol solution has drained through the filtering crucible, the transfer of the sample is continued with water only. The nickel crucible and rod are removed, scrubbed, and washed with water. Washing of the contents of the filter crucible is continued with water until the washings show no alkalinity when tested with indicator paper. The residue is then dried at 110° C., cooled, and weighed. As the fusion in nickel crucibles usually results in some foreign matter remaining in the sample, the polystyrene must be dissolved from the crucible to obtain its correct weight. The crucible is filled about four times with warm carbon tetrachloride, which is allowed to drip through slowly. After thorough washing, the crucible is sucked dry, dried at 110° C., then cooled and reweighed. Loss in weight from washing with carbon tetrachloride is taken as polystyrene. The crucible with residue from the nickel crucible can be cleaned with concentrated sulfuric acid.

DISCUSSION

Styrene monomer is not measured by either procedure. It does not undergo polymerization under the conditions of test.

In the determination of phthalic anhydride in styrenated alkyd resins, the saponification must be carried out as described by refluxing the resin with alcoholic potassium hydroxide; the oven method (*1*) is unsatisfactory. It will cause high results in the phthalic analysis and low results in the polystyrene determination. The alcoholic potassium hydroxide used should be freshly made and free of excessive yellow color, such as is obtained by using alcohol that has been exposed to air or contains appreciable aldehydes. The yellow color is absorbed by the polystyrene and will affect results.

Oil acids may be determined on the filtrate from the separation of the polystyrene in both methods. To determine the oil acids, the filtrate is heated in a water bath until the methanol is removed, then acidified, and the oil acids are extracted with ether as in the usual procedure.

The method outlined for epoxy resins, in which the dried resin reacts with melted potassium hydroxide, is very effective in eliminating interference from most other unsaponifiable resins. By this method, the only resins found to interfere are coumarone-indene and petroleum hydrocarbon resins. Qualitative tests for these two resins are not necessary, as their presence is readily recognizable by the dark brown or black, gummy residue found mixed with the white or near-white particles of separated poly-

styrene at the time of filtration. As their presence affects the weight of the separated polystyrene, no means has been found as yet of preventing their interference in the analysis. Resins likely to be used as modification of the alkyds and found not to interfere in the analysis for polystyrene are rosin and rosin ester, acrylic resins, phenylphenol formaldehyde, and other phenolic resins.

Accuracy. In an effort to check the accuracy of the method, three styrenated oils were prepared with special attention to accuracy of composition. A styrenated dehydrated castor oil was prepared with catalyst and a styrenated blown soybean oil without catalyst.

Dehydrated castor oil (6.141 grams), 4.961 grams of styrene monomer, and 0.111 gram of benzoyl peroxide (as catalyst) were weighed together into a 50-ml. round-bottomed flask equipped with side-arm thermometer and reflux condenser by means of ground-glass joints. The temperature of the mixture was gradually increased to 220° C., at which it remained constant. After 10 minutes it was cooled and 9.291 grams of xylene were added. The mix was then warmed to effect solution and recooled. The nonvolatile matter was determined by drying 1-gram samples in an oven at 110° C. for 3 hours. Considering the volatile to be xylene and unreacted styrene, a nonvolatile composition of 50.75% indicated a polymerized styrene content of 39.9%. Using the method outlined for styrenated alkyds, this sample analyzed 39.7% styrene.

The styrenated blown soybean oil was prepared in a similar manner, omitting the catalyst.

Blown soybean oil (7.000 grams) and 6.994 grams of styrene monomer were weighed together and the temperature was increased slowly over a 3-hour period to 110° C., then to 185° C. in another 2 hours, where the temperature remained constant. After cooling, 13.581 grams of xylene were added and solution was effected. A nonvolatile content of 49.5% indicated 48.7% polymerized styrene content. This sample analyzed 48.1% styrene.

In addition, two manufacturers' samples, each stated to contain 39% styrene, analyzed 39.4, 39.0, and 39.1% in one case and 40.0, 40.1, and 39.9 in the other. A styrenated epoxy resin with known styrene content of 33.3% analyzed 33.8, 33.5, 34.0, and 33.6%.

In an effort to determine the effect on the method of the so-called "copolymer" formed by reaction of styrene and oils of high conjugated unsaturation content, tung oil and styrene monomer were heated together without solvent or catalyst under conditions believed to favor the formation of copolymer and minimize the formation of neutral polystyrene; 13.146 grams of tung oil and 12.719 grams of styrene monomer were mixed in a small flask provided with thermometer and reflux condenser, and the temperature was slowly increased to 170° C. over a period of 6 hours. Higher temperatures yield products insoluble in the usual solvents. On cooling it was found that the product was 66.7% nonvolatile, indicating the presence of 15.9% polymerized styrene. This sample analyzes 16.7% by the method outlined. The results show greater inaccuracy than the other styrenated oils but represent a product that is not encountered commercially, owing to its instability.

These data do not indicate the extent or nature of copolymer formation, or reveal the effect of saponification on such copolymers, but are presented to demonstrate the results of applying the procedure to a variety of styrenated products. Analysis by infrared spectroscopy indicates the presence of small quantities of acid carbonyl groupings in the separated polystyrene of all samples tested, including the styrenated alkyds. Occluded oils or their soaps could be as responsible for this phenomenon as copolymer formation. The acid number of the separated polymer from all samples tested varies from 2 to 5. The agreement between styrene content by analysis and the theoretical composition indicates that any error due to styrene-oil copolymers is not greater than ± 1% on a nonvolatile basis. These investigations indicate that very little, if any, styrene-oil copolymers are formed, or their effect on the analysis by the methods outlined is negligible. The oil acids of alkyd resins, after separation of the styrene, possess their usual properties. If any appreciable quantity of copolymer passes into the filtrate from the polystyrene determination, it is not extracted with ether as are the oil acids. Copolymer formation does not appear to affect the accuracy of the determination of oil acids, but this could be given further study. The polystyrene isolated from oils and resins, when heated in a borosilicate glass test tube, exhibits the complete distillation, negligible char, and odor characteristic of pure polystyrene. Styrenated alkyd samples analyzed by the saponification and the fusion procedures yield the same percentage of polystyrene. Pure polystyrene plastic, dissolved and put through the procedures, is recovered 100%.

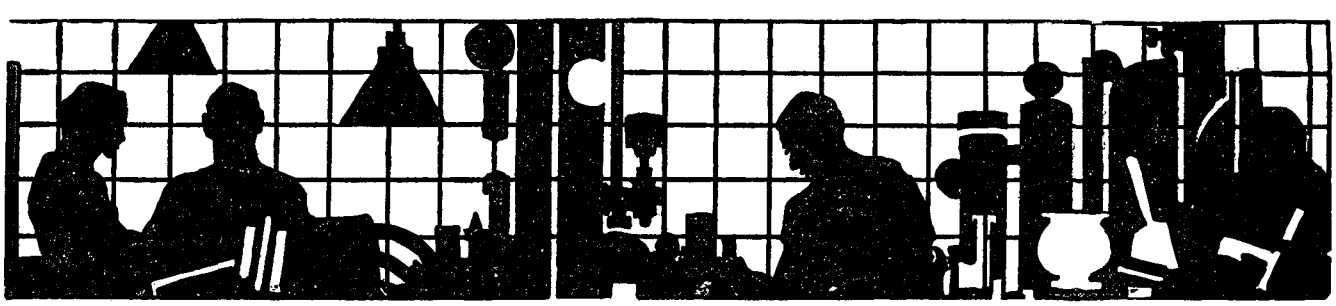
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LITERATURE CITED

(1) Federal Specification TT-P-141b, Method 702.1, Procedure B.
(2) Military Specification MIL-E-10687.
(3) Military Specification MIL-E-10687A.

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Direct Microdetermination of Sodium, Potassium, and Calcium

In a Single Biological Specimen

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This investigation was undertaken to develop a practical flame photometric method for the microdetermination of sodium, potassium, and calcium in a single biological preparation. The use of the photomultiplier tube attachment with the Beckman DU flame photometer permits the selection of narrow slit widths of light, which eliminates nonspecific spectral emission in the flame photometric determination of sodium, potassium, and calcium, when these cations and others are present. Excellent measurement and recovery were obtained from specimens of serum and urine in which extreme ratios of sodium, potassium, calcium, cholesterol, phosphorus, glucose, and urea were present.

SEVERAL procedures have been described for the use of the Beckman DU flame photometer for the quantitative determination of sodium and potassium (*1, 3, 7, 13, 14*) and calcium (*8, 11*) in serum and other body fluids. All reports of the direct determination of calcium in serum by flame photometry have some correction factors for the interference of the spectra of other cations. The determination of calcium on protein-free filtrates of serum (*11*) requires the preparation of elaborate correction curves for the effect of light due to sodium and potassium. Some loss of calcium also occurs with serum protein in the preparation of protein-free filtrates (*3*). Acid digestion, oxalate precipitation, and re-solution of calcium oxalate (*8*) are too tedious and time-consuming for a rapid routine determination of calcium. The Perkin-Elmer flame photometer has been used for the determination of sodium and potassium in biological fluids (*2, 6, 9, 10*), but its use for the determination of calcium has not been reported. Other reports (*4, 5, 12*) have indicated the errors and difficulties of the flame photometric determination of serum calcium.

The method reported in this paper avoids the usual errors and difficulties of flame photometry by use of the photomultiplier tube and narrow slit widths which eliminate the spectral interference of other compounds present. A simple direct method, employing the Beckman DU flame photometer with photomultiplier tube attachment, is presented, in which sodium, potassium, and calcium are determined accurately on a single 0.2-ml. specimen of serum without the use of correction factors.

DIRECT FLAME PHOTOMETRIC DETERMINATION OF SODIUM, POTASSIUM, AND CALCIUM

Reagents. MIXED STOCK STANDARD (150 meq. per liter of sodium, 5 meq. of potassium, and 5 meq. of calcium). Dissolve 0.2496 gram of C.P. Iceland spar (calcite, calcium carbonate, Baker & Adamson) in 10 ml. of concentrated hydrochloric acid in a 1-liter volumetric flask, and dilute to about 500 ml. with distilled water. Add 8.7690 grams of dry C.P. sodium chloride and 0.3728 gram of dry C.P. potassium chloride. Dissolve and dilute to 1 liter with distilled water at room temperature. Store in a tightly stoppered polyethylene or other plastic bottle. Sodium and potassium chloride used in the preparation of this standard should be dried at 100° C. for 2 hours and cooled in a desiccator before weighing..

SODIUM STANDARD (100 meq.). Add 2 ml. of mixed stock standard to 1 ml. of 0.02% Sterox (Sterox, S.E., Monsanto Chemical Co., St. Louis, Mo.) and mix.

STEROX SOLUTION. Dissolve 0.2 ml. of Sterox (0.02%) in 1 liter of distilled water.

Procedure. PREPARATION OF SPECIMEN AND STANDARD. Use only fresh unhemolyzed serum. Serum may be kept refrigerated overnight if separated within 30 minutes from cells and blood clots.

Add 0.2 ml. of serum, with "pipet calibrated to contain," to 10 ml. of 0.02% Sterox in an acid-washed test tube and mix. Wipe off tip of pipet with cotton before inserting into Sterox solution. Fill and wash out pipet three times with the solution.

Prepare a working standard by adding 0.2 ml. of mixed stock standard solution to 10 ml. of 0.02% Sterox for determination of sodium, potassium, and calcium. Prepare an additional standard for sodium determination by adding 0.2 ml. of 100-meq. sodium standard solution to 10 ml. of 0.02% Sterox.

PREPARATION OF FLAME PHOTOMETER. (Check for closure of oxygen and fuel gages of flame photometer before and after using photometer.)

Set fuel (acetylene) tank gage at 10 pounds' pressure.

Set oxygen tank gage at 20 pounds' pressure.

Set flame photometer oxygen gage at the manufacturer's recommended pressure (10 to 17 pounds).

Light a match and quickly set the flame photometer fuel gage at 2 to 3 pounds' pressure, light with match slightly at side, just above burner tip, and make final adjustment of pressure to 5 to 8 pounds. (If flame goes out, quickly turn off fuel to zero pressure and relight match before setting fuel pressure.)

DETERMINATION OF SODIUM. Plug in photomultiplier tube (1P28), set 22-megohm resistance switch, and pull out blue phototube knob.

Turn on switch to 0.1 sensitivity setting.

After a few seconds bring galvanometer needle to null point with dark current knob.

Set light wave-length knob at 590 mμ.

Set slit width knob at 0.01 mm. (0.03 mm. if blue phototube is used).

Set blank (4 ml. of 0.02% Sterox) in 5-ml. cup under burner with elevator lever and set % *T* scale at zero. Turn on phototube switch and zero null point needle by adjusting dark current. Turn off phototube switch.

Pour about 4 ml. of 150-meq. sodium standard in 5-ml. cup and place under burner with elevator lever. Turn on phototube switch.

While 150-meq. sodium standard is burning, set % *T* scale at 75 and zero null point needle by adjusting sensitivity knob. Set 100-meq. sodium standard at 62.5% *T* in the same manner. Turn off phototube switch.

Check standards and blank again as described above.

Place unknown (4 ml.) in 5-ml. cup under burner with elevator lever, and turn on phototube switch and zero null point needle by adjusting % *T* knob. Turn off phototube switch. Observe % *T* and record. Make repeated readings if standards or unknown do not check, or if there appears to be some drift of the null point needle.

CALCULATION

$$Rs \times 2 - (Rs - Ru)\,4 = \text{meq. of Na}$$

or

$$4Ru - 2Rs = \text{meq. of Na}$$

$$4Ru - 150 = \text{meq. of Na}$$

where Ru = reading of unknown and Rs = reading of 150-meq. sodium standard.

This empirical formula has been derived from the slope of the standardization curve for convenience of calculation. If the 100-meq. sodium standard does not read approximately 62.5% T, this formula cannot be used and the unknown must be interpolated from the two standards. However, this formula has been found to hold with different instruments and different dilutions (1 to 50 or less) of specimens and standards for all sodium values between 100 to 200 meq. Because of the constancy of the slope of the sodium standardization curve only one sodium standard, 150 meq., has been used routinely.

The calculation formulas are valid only for sodium concentrations between 100 and 200 meq. Sodium values outside this range should be read from a standardization curve (Figure 1) prepared with standards in the range of concentrations of the unknown to be measured.

Determination of Potassium. Set 10,000-megohm switch and push in phototube-lamp knob to set red phototube in proper position.

Turn on switch to 0.1 sensitivity setting.

After a few seconds zero null point needle with dark current knob.

Set light wave-length knob at 770 mμ light transmittance.

Set light slit width knob at 0.5 mm. or less. Then continue as directed for determination of sodium. Set standard at 50% transmittance, omitting the use of the 100-meq. sodium standard

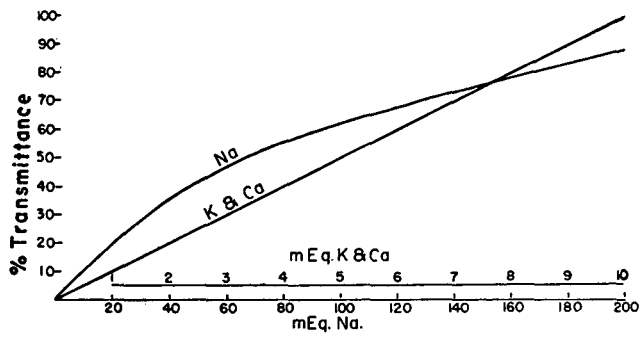


Figure 1. Standardization Curves for Beckman DU Flame Photometer

Prepared by diluting 0.2 to 4.0 ml. of a 1 to 10 dilution of a mixed stock standard in 0.02% Sterox containing 150 meq. of Na, 5 meq. of K, and 5 meq. of Ca per liter, with 0.02% Sterox. Sodium standards were run at 15-meq. and potassium and calcium at 1-meq. intervals.
All standardization points fell on lines indicated.
Sodium. Photomultiplier tube, 590 mμ, slit width 0.01 mm. Blue phototube, 590 mμ, slit width 0.03 mm.
Potassium. Red phototube, 770 mμ, slit width, 0.5 mm.
Calcium. Photomultiplier tube, 422.7 mμ, slit width 0.05 mm. Red phototube, 625 mμ, slit width 0.5 mm.

Calculation.

$$Ru/10 = \text{meq. of K}$$

Determination of Calcium. Plug in photomultiplier tube (1P28). Set 22-megohm resistance switch and pull out blue phototube knob.

Turn on switch to 0.1 sensitivity setting.

After a few seconds zero null point needle with dark current knob.

Set light wave-length knob at 422.7-mμ light transmittance.

Set slit width knob at 0.05 to 0.1 mm. or less. Then continue as directed for determination of sodium. Set standard at 50% transmittance, omitting the use of the 100-meq. sodium standard.

Note. Greater sensitivity for calcium is obtained by using lower oxygen pressure of 10 to 12 pounds and higher acetylene pressure of 7 to 8 pounds.

Calculation.

$$Ru/10 = \text{meq. of Ca}$$

Note. Volume of standard and unknown solutions should be kept approximately equal when all readings are made in the determination of sodium, potassium, and calcium.

Repeated standardizations with new or old burners, using the single standards as described in the procedure, have indicated the constancy of the slope of the standardization curves (Figure 1). Sodium standardization curves prepared with the blue phototube and the photomultiplier tube were identical in slope. The slope of the calcium standardization curve was also identical, whether prepared with the photomultiplier tube or red phototube. However, the photomultiplier tube produced 4 points deflection and the blue tube 1 point deflection of the null point needle with 1% change in transmittance.

Recovery Experiments. Pooled normal serum was diluted with 0.02% Sterox (2 to 1) to obtain a specimen containing 100 meq. of sodium, 3.0 meq. of potassium, and 2.8 meq. of calcium. One to 10 ml. of a 1 to 50 dilution of mixed stock standard in 0.02% Sterox was added to 0.2 ml. of the diluted serum preparation. All specimens were diluted to a final volume of 10.2 ml. with 0.02% Sterox before measurement in the flame photometer.

Good recoveries of sodium, potassium, and calcium added to the serum were obtained (Table I).

The direct determination of calcium in 0.2 ml. of serum with the photomultiplier tube was compared to the oxalate precipitation method in which the red phototube was used. Good agreement between the two methods was found (Table II).

Table I. Recovery of Sodium, Potassium, and Calcium Added to Pooled Serum

Sodium			Potassium			Calcium		
Added,	Recovered		Added,	Recovered		Added,	Recovered	
meq.	meq.	%	meq.	meq.	%	meq.	meq.	%
0	100[a]	...	0	3.00[a]	...	0	2.80[a]	...
15	115	100.0	0.5	3.50	100.0	0.5	3.30	100.0
30	130	100.0	1.0	4.00	100.0	1.0	3.80	100.0
45	146	102.0	1.5	4.50	100.0	1.5	4.30	100.0
60	160	100.0	2.0	5.05	102.5	2.0	4.80	100.0
75	174	98.7	2.5	5.50	100.0	2.5	5.35	101.9
90	190	100.0	3.0	5.95	98.4	3.0	5.85	101.5
105	204	99.1	3.5	6.50	100.0	3.5	6.30	100.0
120	220	100.0	4.0	7.00	100.0	4.0	6.80	100.0
135	234	99.3	4.5	7.55	101.0	4.5	7.25	98.9
150	245	96.7	5.0	8.00	100.0	5.0	7.75	99.0

[a] Present in diluted serum.

DETERMINATION OF CALCIUM BY OXALATE PRECIPITATION AND FLAME PHOTOMETRY

Procedure. Preparation of Standard. Dissolve 0.2496 gram of C.P. Iceland spar in 1 liter of 1 N acetic acid. Add 1 ml. of the standard solution to a selected centrifuge tube containing 1 ml. of 1 N ammonium hydroxide, 1 ml. of 4% ammonium oxalate, and 1 ml. distilled water.

Preparation of Serum or Urine. Add 1 ml. of serum (should be separated from clot or cells 30 minutes after blood is drawn) to a selected fine-point acid-washed 15-ml. borosilicate glass centrifuge tube containing 2 ml. of distilled water and 1 ml. of 4% ammonium oxalate. If urine contains over 15 mg. % of calcium, use 0.5 ml. instead of 1 ml.

Preparation of Blank. Add 1 ml. of 1 N acetic acid to a selected centrifuge tube containing 1 ml. of 1 N ammonium hydroxide, 1 ml. of 4% ammonium oxalate, and 1 ml. of distilled water.

Precipitation and Solution of Oxalate for Measuring Emission Spectra of Calcium. Mix the serum, standard,

Table II. Determination of Calcium in Serum of Hospital Patients

Specimen No.	Direct, Mg. %	Oxalate Ppt., Mg. %
1	9.2	9.3
2	8.0	7.8
3	9.4	9.6
4	8.8	8.6
5	9.7	9.7
6	9.4	9.6
7	7.6	7.4
8	9.3	9.4
9	9.7	9.5
10	9.4	9.2
11	8.6	8.4
12	9.4	9.4
13	9.4	9.6
14	9.6	9.4
15	9.2	9.2
16	8.6	8.4
17	9.2	9.0
18	8.4	8.4
19	9.4	9.2
20	9.0	8.8
21	9.0	9.0

and blank tubes thoroughly by twirling tube vigorously until mixing is complete. Let stand 2 hours for complete precipitation. Centrifuge tubes 10 minutes at 3000 r.p.m. In one continuous motion carefully decant the supernatant fluid and allow tubes to drain inverted on a sheet of filter paper for 5 minutes. Hold tubes in verted and wipe out mouth with filter paper strips. (Do not let precipitate dry completely, as difficulty may be experienced in dissolving.) Moisten oxalate precipitate with 1 drop of 50% hydrochloric acid and add 5 ml. of 1 *N* acetic acid with a forced stream from pipet to bring precipitate into suspension. Place stoppered tubes in a boiling water bath for 5 minutes to effect solution. Cool contents of tubes to room temperature. Read the solutions on flame photometer with the blank set at 0% *T* with 625 mμ light transmittance. Set the 0.10-mg. calcium standard at 50% *T* and read the unknown immediately after this setting without any additional change of controls of the instrument. Recheck standard after reading each unknown.

CALCULATION

$$Ru/10 = \text{meq. of Ca}$$

Good recoveries of calcium added to serum, plasma, and urine were obtained by the oxalate precipitation method. The data of Table III were obtained without use of the photomultiplier tube attachment, using a light transmittance of 625 mμ.

EFFECT OF SERUM CONSTITUENTS ON EMISSION SPECTRA

Sodium and Potassium. BLOOD. Thirty to 150 meq. of sodium and 0.5 to 5.0 meq. of potassium were added to a series of 51 pooled serums which contained 15 to 415 mg. % of urea nitrogen, 36 to 536 mg. % of glucose, and 160 to 1160 mg. % of cholesterol. Then 0.1, 0.2, 0.3, and 0.4 mg. of urea, 0.2, 0.4, 0.6, 0.8, and 1.0 mg. of glucose, 0.4, 0.8, 1.2, 1.6, and 2.0 mg. of cholesterol, 0.06, 0.12, 0.18, 0.24, and 0.30 meq. of sodium, and 0.002, 0.004, 0.005, 0.006, 0.008, and 0.01 meq. of potassium were mixed in these concentrations in nearly all possible different combinations (over 2000 determinations) with each other and added to 0.2 ml. of serum containing 0.03 mg. of urea nitrogen, 0.18 mg. of glucose, 0.32 mg. of cholesterol, 0.0284 meq. of sodium, and 0.009 meq. of potassium.

Recoveries of 96.7 to 103.2% were obtained for added sodium and 98 to 104% for added potassium. The addition of 1000 mg. % of cholesterol contributed to the potassium spectra to give an apparent recovery of 104%.

URINE. Five to 200 meq. of sodium and 5 to 100 meq. of potassium were added to a series of 161 pooled urines which contained 1000 to 4000 mg. % of urea nitrogen, 0 to 6000 mg. % of glucose, and 100 to 500 mg. % of phosphorus (added as mono- and dibasic sodium salts); 1.0, 2.0, 3.0, 4.0, 5.0, and 6.0 mg. of urea nitrogen, 2.0, 4.0, 6.0, 8.0, 10.0, and 12.0 mg. of glucose, 0.02, 0.2, 0.4, 0.6, and 0.8 mg. of phosphorus, 0.01, 0.02, 0.03, 0.05, 0.1, 0.2, 0.3, and 0.4 meq. of sodium, and 0.01, 0.02, 0.04, 0.08, 0.12, 0.15, and 0.2 meq. of potassium were mixed in these concentrations in nearly all possible different combinations (over 2000 determinations) with each other and added to 0.2 ml. of urine containing 2.0 mg. of urea nitrogen, 0.2 mg. of glucose, and 0.2 mg. of phosphorus.

Recoveries of 98 to 101.3% were obtained for added sodium and 98.0 to 102.3% for added potassium.

Calcium. BLOOD. The addition of 15 to 150 meq. of sodium, 0.5 to 5.0 meq. of potassium, and 0.5 to 5.0 meq. of calcium to 44 pooled human serums together or separately in nearly all possible combinations of these concentrations (over 500 determinations) permitted good recoveries of calcium by both the direct and the oxalate precipitation methods. The addition of 5 to 20 mg. of phosphorus as mono- or disodium salts to 100 ml. of serum produced no measurable effect on the recovery of 0.5 to 5 meq. of calcium added to pooled serums containing the added phosphorus.

URINE. Thirty to 150 meq. of sodium, 10 to 50 meq. of potassium, and 50 to 500 mg. % of phosphorus were added in nearly all possible combinations of these concentrations (over 500 determinations) to 44 pooled urines to which 0.5 to 5 meq. of calcium was added for recovery.

The per cent of recovery of calcium ranged from 96 to 102%, indicating that the variation of these constituents in urine has little appreciable effect on the emission spectra of calcium under the conditions used in the method.

SENSITIVITY KNOB AND SLIT WIDTH SETTINGS OF PHOTOMETER

Sodium. Under the conditions described for the direct determination of sodium, in 0.2 ml. of serum (1 to 50 dilution) a 0.01-mm. slit width with photomultiplier tube and a 0.03-mm. slit width with the blue phototube are recommended. The sensitivity knob set at one half to maximum sensitivity was found most satisfactory to keep per cent transmittance readings within range for reading on the scale of the instrument and to obtain approximately 3- to 4-point deflection of null point needle for each unit of per cent transmittance.

Potassium. Strong interference of the potassium spectrum by sodium was observed above slit widths of 0.7 mm. (0.5 is recommended), resulting in incorrectly high potassium values. The sensitivity knob was set at a maximum.

Table III. Recovery of Calcium by Oxalate Precipitation Method

(Calcium added to 1 ml. of serum containing 0.090 mg. of calcium, 1 ml. of plasma containing 0.006 mg. of calcium, and 1 ml. of urine containing 0.110 mg. of calcium. Beckman DU photometer, 625 mμ, slit width 0.5 or less)

Sample No.	Serum			Plasma			Urine		
	Added, mg.	Recovered Mg.	Recovered %	Added, mg.	Recovered Mg.	Recovered %	Added, mg.	Recovered Mg.	Recovered %
1	0.01	0.010	100.0	0.02	0.020	100.0	0.01	0.010	100.0
2	0.02	0.020	100.0	0.05	0.050	100.0	0.02	0.020	100.0
3	0.03	0.030	100.0	0.07	0.070	100.0	0.03	0.030	100.0
4	0.04	0.040	100.0	0.10	0.100	100.0	0.04	0.040	100.0
5	0.05	0.050	100.0	0.12	0.120	100.0	0.05	0.049	98.0
6	0.06	0.060	100.0	0.15	0.150	100.0	0.06	0.060	100.0
7	0.07	0.070	100.0	0.17	0.168	98.8	0.07	0.069	98.5
8	0.08	0.080	100.0	0.20	0.196	97.8	0.08	0.078	97.4
9	0.09	0.089	98.8				0.09	0.087	96.6
10	0.10	0.098	98.0				0.10	0.094	94.0

Calcium. Slit widths above 0.1 mm. permitted a portion of the sodium spectra to be measured as calcium. The sensitivity knob was used as described for measurement of sodium.

Linearity of Per Cent Transmittance Curves. A curve (Figure 1) was obtained for sodium between 0 and 100 meq. but a straight line was observed between 100 and 200 meq., from which sodium could be calculated by use of formulas described if standard is set at 75% *T*. Both potassium and calcium gave straight-line curves (Figure 1) when concentration was plotted against per cent transmittance.

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Determination of Fluorides

Spectrophotometric Adaptation of Method of Association of Official Agricultural Chemists

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THE increasing prevalence of fluoridation of communal water supplies has brought the determination of fluorine content of foods to a routine level in some laboratories. A method commonly employed is that of the Association of Official Agricultural Chemists (*1*), as reported by Clifford (*3*), and based on the studies of Dahle *et al.* (*4*). This so-called back-titration procedure involves matching the colors of a blank and the sample by a visual method and depends largely on the ability of the analyst to distinguish colors. The procedure also requires mixing the contents of the tubes several times during the titration, which makes it both time-consuming and bothersome.

A series of investigations conducted in these laboratories resulted in the development of a spectrophotometric method for the determination of fluorides after prior isolation from food samples by the usual procedures. The proposed method is based on the principle of bleaching the thorium-alizarin lake by fluoride ions.

REAGENTS

Stock Solutions. Hydrochloric acid, 0.1 *N*
Hydroxylamine hydrochloride, 1% aqueous solution
Alizarin sodium monosulfonate, 0.1% aqueous solution
Thorium nitrate tetrahydrate [$Th(NO_3)_4.4H_2O$], 0.05% aqueous solution

Standard sodium fluoride solution containing 10 micrograms of fluoride ion per milliliter. The solution is prepared as follows: The sodium fluoride content of a commercial C.P. sodium fluoride powder is determined by precipitation as calcium fluoride (*6*); 2.2105 grams of sodium fluoride (100% basis) are dissolved in distilled water in a 1-liter volumetric flask and made to volume. Ten milliliters of this solution are diluted to 1 liter with distilled water to give the final standard solution.

Color Reagent. Hydrochloric acid, 10 ml.
Hydroxylamine hydrochloride, 10 ml.
Alizarin sodium monosulfonate, 40 ml.
Thorium nitrate, 40 ml.

Color reagent must be freshly prepared. The components are added in the sequence listed. The hydroxylamine was included, as recommended by the AOAC (*3*) method, in order to discharge traces of chlorine which might be found in the distilled samples, due to decomposition of the perchloric acid used in the distillation. The amount of hydrochloric acid was chosen so as to give a pH of 2.75 in the final solution. Dahle *et al.* (*4*) found that at this pH small changes do not influence the titer of the thorium nitrate solution—i.e., the ratio of fluorine to thorium—and hence they do not affect the intensity of the color.

PROCEDURE

The fluorides are isolated from the food samples by the usual procedure of either single or double distillation, with all the precautions concerning interfering substances such as phosphates, sulfates, and chlorides. The distillation is conducted in a constant temperature still as described by Huckabay, Welch, and Metler (*5*). The final distillate is carefully neutralized with 0.05 *N* potassium hydroxide using *p*-nitrophenol as indicator.

Aliquots of the distillates containing from 0 to 50 micrograms of fluoride ion are pipetted into 50-ml. volumetric flasks. Standards containing 0, 10, 20, 30, 40, 50, and 500 micrograms of fluoride ion are prepared for each series of assays. Ten milliliters of the color reagent are added to each flask. The flasks are made to volume with distilled water, stoppered, shaken, and allowed to stand for 2 hours.

The light absorbance at a wave length of 525 mμ is determined by means of a Beckman Model DU spectrophotometer equipped with 10-mm. Corex cells, using a slit width of 0.018 mm. The instrument is set for 100% transmittance with the 500-microgram standard.

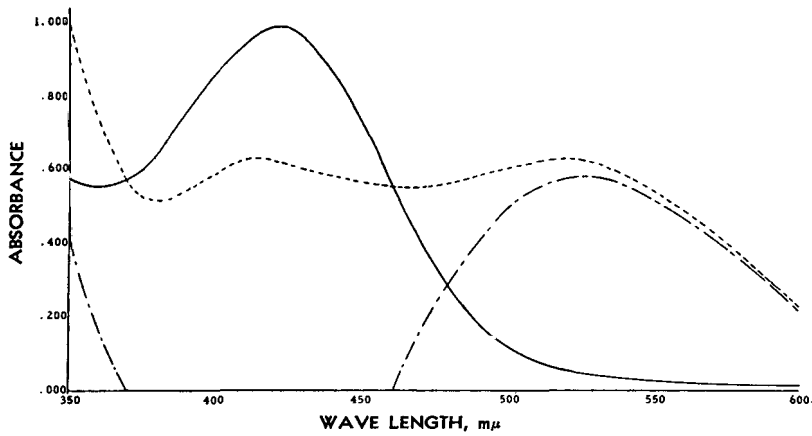


Figure 1. Spectral Absorbance of Thorium-Alizarin Lake

--------, Curve *a* ———, Curve *b* —·—·, Curve *c*

DISCUSSION

The reason for employing the bleached standard (500 micrograms of fluoride) in setting the instrument will be evident from Figure 1. Curve *a* represents the unbleached lake (standard 0) read against distilled water. Curve *b* corresponds to the bleached standard read against distilled water. Curve *c* shows the absorbance of the 0 microgram standard as read against the bleached standard. It will be observed that the last curve has a sharp absorption maximum at 525 mμ.

Figure 2 shows a typical standard curve obtained with the described procedure. Absorbance readings were taken at 525 mμ. This curve has been extended to include points to 100 micrograms per flask. As evidenced by the curve in Figure 2, the

Table I. Effect of Development Period on Light Absorbance

Hours	Absorbance at 525 mμ: Fluoride, 0γ	Fluoride, 20γ	Fluoride, 40γ
0	0.586	0.538	0.482
1/4	0.602	0.543	0.485
1/2	0.608	0.546	0.487
1	0.609	0.548	0.488
2	0.609	0.549	0.489
3	0.609	0.549	0.490
4	0.608	0.550	0.490
5	0.609	0.549	0.490

Table II. Reproducibility of Spectrophotometric Procedure

Fluoride, γ per Flask	Absorbance at 525 mμ	
0	0.640	0.639
10	0.600	0.600
20	0.561	0.562
30	0.529	0.529
40	0.499	0.499
50	0.472	0.471

sensitivity decreases slightly for higher concentrations of fluoride ion. Consequently the range from 0 to 50 micrograms of fluoride per flask is recommended.

The intensity of the color changes with time. It is evident from Table I that the color becomes stable after 2 hours development for low concentrations of fluorides. However for concentrations of fluoride ions of 40 micrograms or more per flask, a 3-hour development period is recommended. Table II shows readings obtained on duplicate standards and indicates the high reproducibility of the spectrophotometric method. This procedure allows accurate estimations of fluoride in concentrations as low as 0.05 microgram per milliliter.

As mentioned above, the final distillate is neutralized with potassium hydroxide prior to assay. In order to investigate the effect of potassium ions on the assay the following experiment was undertaken. An amount of potassium (1 ml. of 0.05 *N* potassium chloride), greater than any that might reasonably be expected to be found in an aliquot taken for analysis, was added to a series of standard solutions of fluoride, and the color reagent was added. No significant change in absorbance was observed compared to untreated standards.

Table III. Fluoride Content of Orange Pekoe Teas[a]

Tea Sample	Fluoride Content, P.P.M., as Determined by: Back-titration	Spectrophotometry
A	111.1	112.7
B	83.6	85.1
C	91.4	92.9
D	119.2	119.4
E	128.3	126.9

[a] As received.

MODIFICATION OF COLOR REAGENT FOR DETERMINATIONS WITH PHOTOELECTRIC COLORIMETER

In order to permit determinations to be made with an Evelyn photoelectric colorimeter in which tubes of 22.5-mm. diameter are employed, the color reagent was modified. The composition of the modified reagent is as follows:

Hydrochloric acid, 0.2 *N*, 10 ml.
Hydroxylamine hydrochloride, 2% aqueous, 10 ml.
Alizarin sodium monosulfonate, 0.1% aqueous, 40 ml.
Thorium nitrate tetrahydrate, 0.05% aqueous, 40 ml.

The procedure employed is the same as described above except that 5 ml. of the modified reagent are added to each flask. The range of fluoride concentrations is the same as described for the spectrophotometric procedure. The Evelyn colorimeter is not equipped with a 525 mμ filter; however, the 520 mμ filter was successfully employed.

The colorimetric procedure allows accurate estimation of fluoride in concentrations as low as 0.1 microgram per milliliter.

APPLICATION OF SPECTROPHOTOMETRIC PROCEDURE TO ANALYSIS OF TEAS

The fluoride contents of a series of commercial samples of blended orange-pekoe tea were determined. Distillates prepared by the official procedure were read by the back-titration method and the spectrophotometric method described above. The results are shown in Table III, from which it is seen that excellent agreement was obtained between the two methods.

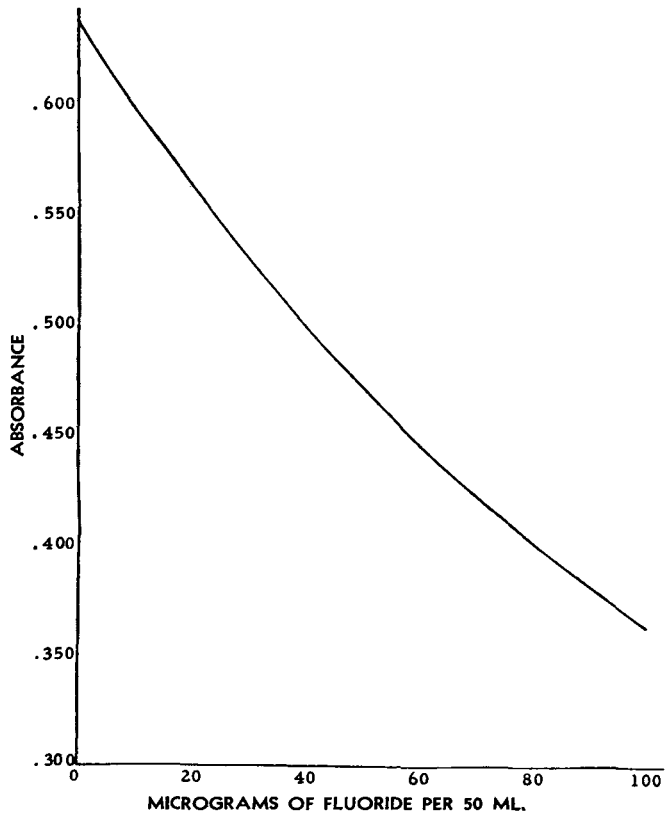


Figure 2. Typical Standardization Curve

CONCLUSIONS

The modified AOAC method presented allows accurate and reproducible estimations of fluorides in concentrations as low as either 0.05 or 0.1 microgram per milliliter depending on whether a spectrophotometer or photoelectric colorimeter is used. It has the advantage that it employs standard laboratory equipment and does not necessitate the use of 20-mm. or 50-mm. cells as required by other published spectrophotometric procedures (*2*).

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Mull and Solvent Media for Infrared Use

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In work on antibiotics, alkaloids, and plant regulators, the samples usually have been solids, and the methods most frequently used to obtain their infrared spectra have involved a medium. This led to frequent concern over what bands may have been obscured by the intense absorptions of the medium. In an earlier presentation and abstract (*1*), media were discussed that would relieve this situation by permitting complete supplementations. Attention was called to the special advantages of a mull system whereby hexachlorobutadiene supplements paraffin oil, and a solution system whereby tetrachloroethylene supplements carbon disulfide. Information concerning the use of these systems is recorded here.

HEXACHLOROBUTADIENE AS A MULL MEDIUM

As shown by the dotted lines of Figure 1, paraffin oil of medicinal grade, as used for most mulls, gives intense obscuring absorptions near 3.4, 6.85, and 7.26 microns. In addition, there are less serious interferences near 2.4, 3.8, and 13.8 microns that often can be ignored but occasionally are disturbing. As shown by the solid line, the transmittance of hexachlorobutadiene exceeds that necessary for supplementation in each of these regions. The thickness in each case is 0.10 mm., which exaggerates the media effects by being roughly three times the thickness of the average mull preparation. It is evident that paraffin and hexachlorobutadiene supplements together can give complete supplementation at mull thicknesses without any interferences of a significant magnitude.

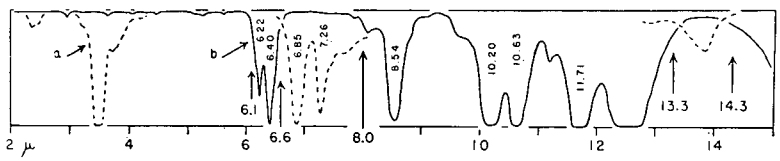


Figure 1. Supplementing Transmittances of Paraffin Oil and Hexachlorobutadiene

A. **Paraffin oil (heavy liquid petrolatum, U.S.P.), 0.10 mm.**
B. **Liquid hexachlorobutadiene, 0.10 mm.**

Perfluorokerosine (*4, 11*) has also been used to obtain spectra that are obscured by paraffin oils, and tests have shown that its useful region extends from below 2 to an absorption edge at about 7.20 microns when the thickness is 0.03 mm. Although the supplementing capacity is adequate for many special purposes, the utility of perfluorokerosine seemed inefficient or doubtful in the 7.3- and 13.8-micron regions, and therefore it was considered to be less complete than that of hexachlorobutadiene. The reduction of light scattering by perfluorokerosine was also believed to be less efficient because compatibilities resulting in partial solution or gelation of the sample seem less likely to occur, and the very low refractive index (n_D^{25} found, 1.3311) probably causes more abrupt changes of refraction at particle interfaces. The cost and availability of perfluorokerosine are also somewhat restrictive. It was concluded, therefore, that hexachlorobutadiene can advantageously replace perfluorokerosine for most mull purposes.

As widespread usage of hexachlorobutadiene has already resulted from the earlier announcement (*1*), it can now be recommended without reservation as a product whose general suitability has been proved by service. It is an oily liquid having a boiling point of 215° at 760 mm., and a refractive index (n_D^{25}) of 1.5542 (*6*). Although the stability may not be as great as that of perfluorokerosine, it far exceeds the requirements. Fruhwirth (*6*) reported that it behaves like a fully saturated compound; he could not polymerize it at 100 atmospheres' pressure, nor would it react with chlorine in the sunlight, with diene reagents like maleic anhydride, or with acids and bases. Other evidence of its unusual stability was reported by McBee and Hatton (*10*). The reagent used here was a commercially available product, of n_D^{25} 1.5524, with the boiling point listed as 210–212°. This product did not need further purification and has shown no evidence of change in 3 years.

Because solubility and other properties specific to the sample are not limiting factors by the mull technique, the single supplementing combination of hexachlorobutadiene and paraffin oil adequately covers the entire general need for media in the mull field. Without further concern over media selections, these may be used to obtain qualitatively useful spectra of nearly every type of dry powderable sample. Highly bonded substances may give spectra that are not as sharp as desired, but this is not due to any fault of the media. Since the intensity of the CH bands as revealed by hexachlorobutadiene often is of understandable significance as a quantitative standard, having these and one additional band that is common to both supplements gives a basis for evaluating all intensities relative to each other, despite losses due to scattering. Although the accuracy is low, such evaluations are useful for estimating if a band is intense enough to indicate a specific group of the principal ingredient, as distinguished from minor bands that may arise from contamination or from secondary effects of fundamental vibrations.

When there is an unusual need to conserve the sample, the hexachlorobutadiene supplement can be done after the paraffin oil supplement on the same sample after the paraffin oil has been carefully flooded off with a volatile rinsing liquid like hexane.

Bonding patterns may be on a simpler basis in hexachlorobutadiene than in a paraffin oil medium, although such differences are of rare occurrence and have not been observed outside the 3-micron region. The most logical explanation seems to be that the hydrogen-containing oil has mild bonding properties, and the imbibing of this oil by the sample may force a change in weakly established bonding equilibria to give additional complexities. Although not observed, it seems reasonable to expect that imbibing an oil could influence the spectra of hydrates by displacing water in some instances.

TETRACHLOROETHYLENE AS AN INFRARED SOLVENT

As reported earlier (*1*), and evident from published spectra (*3, 8, 11*), tetrachloroethylene can fill a critical need as an infrared solvent in the region from below 2 to 7.3 microns. It is possible to supplement completely the favorable region of carbon disulfide from 7.3 to beyond 15 microns. It seems evident, however, that the use of tetrachloroethylene has been hindered by troubles with impurities, and that there is a need to understand and take special precautions against these.

On exposure to light, air, and moisture, the unpreserved material becomes oxidized, resulting in contamination with trichloroacetyl chloride, phosgene, trichloroacetic acid (*5, 7*), and presumably hydrochloric acid. Ordinarily, the access of air in storage is not sufficiently prevented by glass stoppers. After contamination, a simple distillation does not adequately remove trichloroacetyl chloride, as the boiling range is similar. Trichloroacetyl chloride may be detected both by its odor and by a prominent band at 5.56 microns having a subsidiary peak at 5.72.

Commercially available tetrachloroethylene usually already contains a preservative, often about 0.5 to 1% alcohol (*12*), although advantages have been reported for pyrroles (*9*), and for thymol and other compounds (*2*). The purity has been satisfactory for infrared purposes when small portions were distilled as needed from a stock preserved with alcohol in brown bottles, and the first portion distilled was discarded. It seems advisable also to discard the excess remaining after use instead of attempting to preserve it. The need for such attention evidently will greatly restrict the use of tetrachloroethylene until more convenient means of maintaining its purity have been established, but for many purposes the advantages of complete supplementation warrant the extra effort.

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Ultraviolet Spectrophotometric Determination of Antimony as Iodoantimonous Acid

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In a study of the solubility of antimonous oxide it became necessary to determine accurately very low concentrations of antimonous ions. A preliminary study of several colorimetric methods indicated that the iodoantimonous acid method offered advantages in respect to accuracy, precision, and sensitivity. This method is based on the formation of yellow iodoantimonous acid ($HSbI_4$) when trivalent antimony in sulfuric acid solution is treated with an excess of potassium iodide solution (*1*). McChesney (*3*) studied this colorimetric method in reference to the effect of iodide concentration, acidity, and certain diverse ions and applied the method to the determination of antimony in biological materials. He made photometric measurements in the visible region at 425 mμ. Holler (*2*) used the iodoantimonous acid method to determine antimony in copper-base alloys using photometric measurements in the visible region. Nikitina (*4*) also used the iodoantimonous acid method in determining antimony in copper and tin alloys.

The purpose of this investigation was to determine the ultraviolet absorption spectrum of iodoantimonous acid and to find whether it could be used as the basis for a more sensitive spectrophotometric method for the determination of very low concentrations of antimonous ions.

GENERAL EXPERIMENTAL WORK

Apparatus. A Beckman Model DU spectrophotometer with 1.00-cm. silica cells was used for all absorbancy measurements. A hydrogen discharge lamp was used for measurements in the 220- to 400-mμ region and a tungsten filament lamp was used for the 400- to 500-mμ region.

Solutions. A standard antimony solution was prepared by dissolving 0.2743 gram of $KSbC_4H_4O_7.{}^1/_2H_2O$ in redistilled water, adding 160 ml. of concentrated sulfuric acid, and diluting to 1 liter with water. Each milliliter of this solution contains 0.100 mg. of antimony per ml. This concentration was checked spectrophotometrically using a standard solution prepared from pure antimony metal.

Sulfuric acid reagent solutions were prepared by adding concentrated acid to distilled water and diluting to 1 liter.

A potassium iodide solution was prepared by dissolving 140 grams of reagent grade potassium iodide and 10 grams of crystalline ascorbic acid in redistilled water and diluting to 1 liter. The purpose of the ascorbic acid is to reduce any trace of iodine which may be liberated by traces of oxidants, or by actinic rays.

Experimental Procedure. The procedure given below was followed in determining the effect of various solution variables.

A definite amount of the standard antimony solution was transferred to a 50-ml. volumetric flask. The potassium iodide reagent solution was added, followed by the addition of the sulfuric acid reagent. In the case of the diverse ion study, the diverse ions were added before the potassium iodide. The final volume

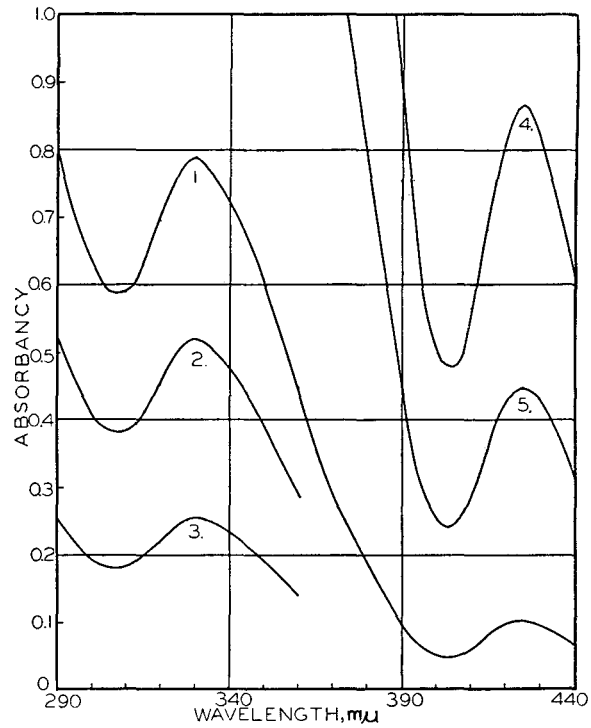


Figure 1. Absorption Spectra for Iodoantimonous Acid

1. 3 p.p.m. antimony
2. 2 p.p.m. antimony
3. 1 p.p.m. antimony
4. 24 p.p.m. antimony
5. 12 p.p.m. antimony

Table I. Interference of Diverse Ions with Determination of Antimony as Iodoantimonous Acid

		Absorbancy Measured at 330 mμ			Absorbancy Measured at 425 mμ		
Ion	Added as	Amt. added, p.p.m.	Amt. found, as p.p.m. Sb	Permissible amt.[a]	Amt. added, p.p.m.	Amt. found, as p.p.m. Sb	Permissible amt.[b]
AsO_3^{---}	Na_3AsO_3	500	0.5	50			[c]
Bi^{+++}	$Bi(NO_3)_3$	2	1.4	0	10	1.65	0
Cu^{++}	$CuSO_4$	20	0	20[d]	20	0	20[d]
Pb^{++}	$Pb(NO_3)_2$	10	1	0	10	0	10[d]
Hg^{++}	$Hg(NO_3)_2$	10	3.4	0			[c]
MoO_4^{--}	Na_2MoO_4	100	0.15	30	100	0	100[d]
Ni^{++}	$NiSO_4$	100	0	100[d]	100	0	100[d]
Sn^{++}	$SnCl_2$	100	0.9	5	100	0	100[d]
WO_4^{--}	Na_2WO_4	50	0.6	4	500	Turbid	100

[a] As p.p.m., causing less than +2.5% error when added to 2 p.p.m. antimony.
[b] As p.p.m., causing less than +2.5% error when added to 10 p.p.m. antimony.
[c] See (3).
[d] Larger amounts caused interference.

was adjusted to 50 ml. The reference absorption cell contained a solution which had the same concentration in respect to sulfuric acid, ascorbic acid, and potassium iodide as the solution under investigation. Absorbancy measurements were made every 2 mμ from 280 to 500 mμ.

SOLUTION VARIABLES

Antimony Concentration. The existence of absorbancy maxima in the ultraviolet and visible regions at 330 and 425 mμ, respectively, permits spectrophotometric measurements to be made at two wave lengths. The ratio of the absorbancy index at 330 mμ to the absorbancy index at 425 mμ is 7.50, which indicates that the sensitivity is increased 750% if the absorbancy measurements are made at the ultraviolet absorbancy maximum. Conformity to Beer's law was observed at 425 mμ for 0 to 25 p.p.m. of antimony and at 330 mμ for 0 to 4 p.p.m. of antimony. The optimum concentration range is 0.3 to 3.5 p.p.m. of antimony when measurements are made at 330 mμ and approximately 3 to 25 p.p.m. of antimony at 425 mμ. When concentrations are larger than 25 p.p.m. of antimony, it is advisable to prepare a calibration graph. Figure 1 shows the effect of antimony concentration of the ultraviolet absorbancy maximum and a comparison of the magnitude of absorbancy maximum in the visible and ultraviolet regions. The spectral slit width was maintained at 5.5 mμ for measurements at 330 mμ and at 1.25 mμ for 425 mμ.

Acid Concentration. The effect of sulfuric acid concentration was studied using 2 p.p.m. of antimony when spectrophotometric measurements were made at 330 mμ and using 14 p.p.m. of antimony at 425 mμ. Variable amounts of an 18 *N* sulfuric acid were added to give various acidities. The acidity due to the sulfuric acid in the standard solution was taken into consideration in computing the final acidity. The final acidity should be 2.4 to 3.8 *N* in respect to sulfuric acid, regardless of whether measurements were made at 330 or 425 mμ. The final acidity of approximately 2.8 *N* was used in subsequent investigations. This acidity corresponds to that recommended by McChesney (3).

Iodide Concentration. The effect of iodide concentration was also studied using 2 p.p.m. of antimony in spectrophotometric measurements at 330 mμ and 14 p.p.m. of antimony at 425 mμ. The absorbancy as measured at 330 mμ increased until 3 grams of the potassium iodide had been used per 50-ml. final volume. When measurements were made at 425 mμ it was found that 3.5 grams of potassium iodide per 50 ml. were needed to ensure attainment of maximum absorbancy. There is a negligible change in absorbancy when measurements are made at 330 mμ if the final iodide concentration corresponds to 3 grams of potassium iodide per 50 ml. of solution. The recommended iodide concentration is 3.5 grams of potassium iodide per 50 ml. of solution, which corresponds to the use of 25 ml. of the iodide–ascorbic acid reagent. This also results in an ascorbic acid concentration of 0.25 gram per 50 ml. of solution.

The ultraviolet absorption spectrum of the potassium iodide–ascorbic acid reagent was determined; it was found to exhibit negligible absorbancy above 310 mμ.

Stability. The prepared iodoantimonous acid solutions are stable for at least 5 hours.

Diverse Ion Concentration. The effect of diverse ions was studied using 2 p.p.m. of antimony for the ultraviolet spectrophotometric measurements and 10 p.p.m. of antimony at 425 mμ. An error of less than 2.5% was considered negligible. For the ultraviolet spectrophotometric method it was found that 500 p.p.m. of the following ions did not cause interference: chloride, bromide, nitrate, phosphate, sodium, magnesium, calcium, ammonium, zinc, cadmium, aluminum, manganous, ferrous, and cobaltous. It was found that 200 p.p.m. of germanium did not interfere.

For the visible spectrophotometric method 500 p.p.m. of the following ions did not cause interference: chloride, bromide, nitrate, phosphate, sodium, magnesium, calcium, ammonium, zinc, cadmium, aluminum, manganous, ferrous, cobaltous, arsenite, and mercuric. Those ions causing interference are listed in Table I. Unless otherwise indicated, the interference was due to an increase in absorbancy. Possible methods of circumventing interferences were not studied.

RECOMMENDED GENERAL PROCEDURE

Preparation of Sample. Weigh, or measure by volume, a sample containing sufficient antimony so that the resulting solution contains 0.15 to 1.8 mg. of antimony per 100 ml. of prepared solution. This prepared solution should be slightly acidic with sulfuric acid.

Measurement of Desired Constituent. Transfer a 10-ml. aliquot to a 50-ml. volumetric flask. Add 25 ml. of the potassium iodide–ascorbic acid reagent. Dilute to the mark with a sulfuric acid solution containing 250 ml. of concentrated sulfuric acid per liter. Mix thoroughly and measure the absorbancy at 330 mμ using 1-cm. silica cells and a reagent blank solution in the reference cell.

DISCUSSION

The coexistence of an absorbancy maximum in the ultraviolet region with the previously known absorbancy maximum in the visible region was established for the iodoantimonous acid system. Spectrophotometric measurement in the ultraviolet region results in greatly increased sensitivity. The recommended general procedure using 2 p.p.m. of antimony gave a standard deviation of 3.3% when the absorbancy was measured at 330 mμ. The same procedure using 10 p.p.m. of antimony gave a standard deviation of 1.1% when the absorbancy was measured at 425 mμ. Mercuric, plumbous, and bismuthyl ions are the main interfering substances in the ultraviolet method, while bismuthyl is the main offender in the visible method.

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Mass Spectrometric Determination of Gas Impurities Separable by Condensation

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A METHOD of utilizing an internal standard in the mass spectrometric determination of traces of noncondensable impurities in condensable gases or condensable impurities in noncondensable gases is presented. The preparation and analysis of synthetic mixtures in the range of 30 to 200 parts of impurities per 100,000 parts of main component are described.

The mass spectrometric determination of condensable impurities in noncondensable gases is well known. Recent examples of the use of this method are given in the papers of Washburn and Austin (*10*) and Shepherd, Rock, Howard, and Stormes (*8*) on the concentration and mass spectrometric determination of condensable impurities related to smog in air. Happ, Stewart, and Brockmyre (*4*) have used the method for the determination of condensable vapors in room air. In these cases the combination of system volume and mass spectrometer sensitivity were used to determine the amount of impurity present, relating it to the volume of sample collected.

This method is satisfactory for the study of condensable impurities in noncondensable gases, but does not work as well for the inverse case of noncondensable impurities in condensable gases, where the fraction of gas mechanically entrapped in the large bulk of condensate is unknown. To avoid the difficulty of mechanical entrapment of the noncondensable impurity, it has been found convenient to introduce into the mixture an internal standard of the same gas type as the impurities. The concentration of the added standard is arbitrary and need not be known, but the ratio of main component to internal standard should be easily and accurately measured on the mass spectrometer record, yet the concentration of the standard must be small enough so that after separation by condensation the ratio of impurities to standard can be accurately measured. For an unknown gas mixture this may require a trial blend before a desirable concentration of internal standard is added.

Internal standards in mass spectrometric analyses have been used by Hindin and Grosse (*6*), who introduced neon as an internal standard in the determination of nitrogen, using a modified Dumas technique combined with the mass spectrometer. These authors suggested that the internal standard method might also be used for the analysis of trace impurities but did not extend the work to cover such cases. Grosse, Hindin, and Kirshenbaum (*3*) extended the method to use internal standards of oxygen-18, nitrogen-15, or carbon-13 for the determination of oxygen, nitrogen, and carbon, respectively, in the elementary analysis of organic materials. Thomas and Seyfried (*9*) have used an internal standard of benzene in the analysis of liquid oxygenated compounds.

Selecting Internal Standards. In principle, for the determination of noncondensable impurities in condensable gases the selection of the internal standard to be used is important if solubility effects are to be minimized. Since the system is one containing a small amount of gas in contact with a large bulk of condensate, the solubility characteristics of the internal standard and the impurities should be as nearly identical as possible. In practice, using liquid air or liquid nitrogen as the condensing medium, the choice of internal standard is rather limited, and the best one can do is strike a compromise, particularly if the properties of the impurities range from those of hydrogen to methane. At higher condensation temperatures—e.g., when dry ice or a carbon disulfide slush bath (−111° C.) is used—a wider choice is possible. In the work reported here, liquid nitrogen was the only condensation medium used. For noncondensable impurities, neon was used as an internal standard, chiefly because it bridges the gap in properties between hydrogen and oxygen, nitrogen, and carbon monoxide and has an isolated peak of fair sensitivity at mass 20, which simplifies the calculations.

In the case of condensable impurities in noncondensable gases this solubility problem does not arise and the choice of internal standards is much wider, the major consideration being complete condensation at the temperature used with a minor consideration being the existence of an isolated peak of considerable sensitivity for simplification of the calculations. Any solubility of the gross noncondensable component in the condensate is easily taken care of in the analysis of the condensate spectrum.

EXPERIMENTAL PROCEDURE

All gases used were of the highest purity available, and all condensable gases used as major components were distilled three times in vacuum, pumping on the condensed material with a fast oil diffusion pump after each distillation. All gases were checked for purity with the mass spectrometer, and where the impurities were noninterfering—e.g., 0.2% argon in oxygen—the impurity peaks were considered as part of the gas spectrum. The tank carbon monoxide used in making mixtures was only 97.5% pure; both oxygen and nitrogen were present as impurities, and the amounts of these components were added to the oxygen and nitrogen contents of the gas mixtures. The carbon monoxide used for calibration purposes was synthesized; the mass spectrometer pattern showed no extraneous peaks, and the purity was calculated to be better than 99.8%. Traces of impurities in the neon were considered part of the neon spectrum. Liquids used as condensable impurities were reagent grade quality, used as received. Except for carbon monoxide, the calibration spectra were run with the same materials from which the mixtures were made.

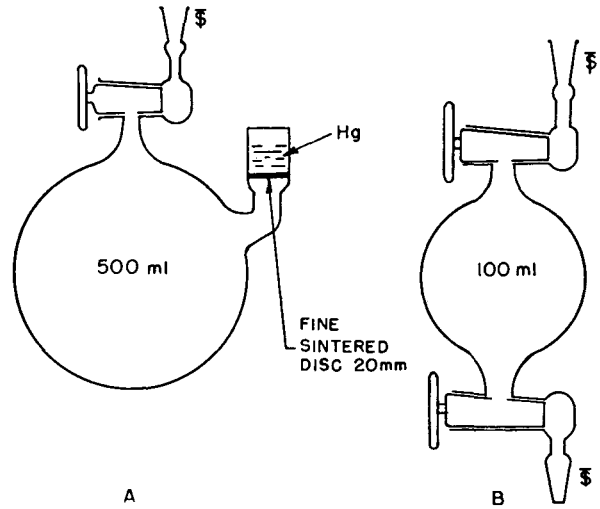


Figure 1. Gas Bottle for Making Mixtures, *A*, and Mixing Bulb for Adding Internal Standards, *B*

Samples of Noncondensable Impurities in Condensable Gases. A 500-ml. gas bottle (shown in Figure 1, *A*) was used for making the mixtures containing known amounts of gases to be used as noncondensable impurities. An inlet sealed to the side of the flask was used for the introduction of the minor components. The inlet was closed with a mercury-sealed sintered disk. The volume of this bottle was accurately measured by comparing helium expansion in it with a standard 300-ml. gas bottle, which had been calibrated by weighing water contained. The volume measurement was accurate to within 0.5 ml.

The stopcocks used both on this bottle and the mixing bulb were high vacuum stopcocks of the hollow-plug type, which eliminated trapping of unequilibrated gas in a stopcock bore.

After evacuation of the gas bottle to better than 10^{-5} mm. of mercury as measured on a McLeod gage, known amounts of each of the noncondensable gases were added through the inlet, using calibrated gas pipets of the type described by Charlet (*1*, *2*). These gas pipets were volume calibrated against the metering volume and micromanometer of the mass spectrometer by making successive introductions of air into the mass spectrometer, first in the regular manner using the metering volume of the spectrometer to get the air sensitivity, and then introducing air with the pipet through the mercury-sealed disk on the spectrometer. Since the metering volume on the spectrometer was calibrated by weighing mercury contained, and the expansion volumes were calibrated by comparison with a standard volume, the absolute pipet volume was known, with accuracy within 1%. The reproducibility of the pipets on successive introductions of air into the mass spectrometer through the mercury-sealed disk was within 0.2%, this being measured by the reproducibility of the heights of the mass 32 and 28 peaks. Therefore, the absolute amounts of noncondensable gases added were known, within 1%.

The condensable gas (main component) was added to the 500-ml. gas bottle from a storage bulb on the vacuum system into which it had been condensed. At the same time, a sample of the condensable gas was collected in another gas bottle on the vacuum line, to be used for calibrating purposes and run later as a check for purity by the same procedures used in analyzing the mixture. The main component was added by opening the cold storage bulb to the vacuum line and blank bottle, removing the cold trap, and allowing the bulb to warm until the pressure in the system approached atmospheric, at which time the stopcock to the 500-ml. gas bottle was then opened slightly. When the pressure again approached atmospheric in the system, in rapid order the storage bulb was shut off, the cold trap replaced, and the stopcock to the 500-ml. gas bottle completely opened for a bare second for pressure equilibration, and then closed. The manometer then showed the total pressure in the gas bottle. Checks on this procedure showed that opening the gas bottle to the line a second time produced no change in the manometer reading. The gas bottle was then alternately gently warmed and cooled on one side to aid in equilibration of the gas. (Caution: warming must be very gentle to prevent loss of gas through the disk and mercury due to pressure increase.) For convenience these mixtures were allowed to stand overnight before proceeding with the analysis though this was probably unnecessary for equilibration using convection mixing.

Samples of Condensable Impurities in Noncondensable Gases. In making up mixtures with condensable impurities in noncondensable gases, liquids were used as condensable gases for convenience of handling. These were introduced into the evacuated mixing bottles via the mercury-sealed disk with Precision Capillary Dippers (*2*, *7*). The volume of the dippers used was calibrated in two ways. Dippers were filled with mercury and emptied into a weighing bottle by suction, weighing 40 dippers of mercury divided into 4 groups of 10 each. Only selected dippers which can be loaded with mercury and hold the load can be calibrated in this manner, but using these as primary standards others can be calibrated by comparison of pentane introductions on the mass spectrometer. In the second method of calibration the dipper volume was compared with the metering volume and micromanometer of the mass spectrometer, using *n*-pentane and introducing it alternately through the metering volume and with the dipper. All methods agreed to within 1% using *n*-pentane. In general, these dippers deliver reproducible amounts of low boiling hydrocarbons, the maximum deviation in 10 successive introductions of *n*-pentane to the mass spectrometer through a mercury-sealed sintered disk being not over 0.4% with a mean deviation of only 0.2%. Measurements with alcohols and other oxygenated compounds are not as reproducible, and successive introductions show deviations as large as 1%. Thus the error on the amount of liquid (condensable component) added was about 1%. The noncondensable component was then added from a large storage reservoir on the vacuum system in the same manner as described above.

Adding Internal Standards. The gas mixtures were blended with the internal standard gas in a mixing bulb of about 100-ml. capacity shown in Figure 1, *B*. This was placed between the gas bottle and the vacuum line, both mixing bulb stopcocks were opened, and the bottle was evacuated to less than 10^{-5} mm. of mercury. The lower stopcock was then closed, and the internal standard gas was added through the vacuum line to a pressure of 8 to 10 mm. (only roughly measured), which represents a suitable concentration of standard for impurities in the range 0.3 to 2 parts per thousand, and for the bottle sizes described. The stopcock to the vacuum line was then closed, that of the gas bottle was opened, and finally the stopcock to the mixing bulb was opened and then closed. It is not necessary to completely equilibrate the pressures, nor is diffusion between the two bottles critical at this point. The mixing bulb was then gently warmed on one side for a few minutes to ensure equilibration of the internal standard and gas mixture in the bulb. In the case of noncondensable impurities in condensable gases, the bulb was ready for the mass spectrometer at this point, but for the condensable impurities in noncondensable gases, part of the blend of internal standard and gas mixture was transferred to a finger-shaped gas bottle, which could be immersed almost completely in liquid nitrogen.

Mass Spectrometric Analysis. The mass spectrometer used was a Consolidated Engineering Corp. model 21-102 converted to model 21-103 except for the inlet system, although the 21-102 inlet system used was provided with a Consolidated Engineering Corp. type 23-105 micromanometer. The spectrometer was operated essentially in accordance with the manufacturer's recommendations. The sensitivity of the instrument can be changed at any time by a switch increasing the ionizing current by a factor of 5, which increases the sensitivity by the same factor, and by a switch changing the grid resistor in the d.c. amplifier from 10^{10} to 10^{9} ohms, which decreases the sensitivity by a factor of 10. In the work reported here only the first method of changing the sensitivity was used, although in principle the analytical range of the method could be extended by using a combination of the two sensitivity changes. Calibration runs on the pure components and internal standard were made at both normal and increased sensitivity (×5), although on the spectrometer used no significant pattern changes resulted from increasing the electron emission as long as the ion source temperature was not allowed to rise appreciably during the run at increased emission; thus the sensitivity factor was the same for all peaks in the spectra of the component gases.

Mass spectrometer runs were made according to the following schedule:

(1) Calibration runs on main component gas at normal and increased sensitivity.

(2) Total gas run, all peaks being recorded at normal sensitivity except those of the internal standard used (neon mass 20 or sulfur dioxide mass 64) which were run at increased sensitivity.

(3) Calibration runs on internal standard at normal and increased sensitivity.

(4) Separated gas run, the separation of noncondensable gases from condensable being made by very slowly bleeding the gas into the mass spectrometer through the liquid air trap on the inlet system. This allowed a trace of the condensable gas to go through the liquid air trap, but this did not interfere in the analysis. The condensable-impurity type mixture was separated by immersing almost the entire finger-type gas bottle in liquid nitrogen for 15 to 20 minutes, then the noncondensable gases were pumped off, the stopcock was closed, and the entire trap was allowed to warm to room temperature before introducing the condensable gas into the mass spectrometer. Trial experiments showed no appreciable fractionation (less than 1%) of components using freezing times of 5 minutes to 1 hour and impurities and internal standard concentrations in the range of the sample used. The separated components were run, scanning all peaks at increased sensitivity except the internal standard peaks which were scanned at normal sensitivity.

(5) Calibration runs on each of the impurity gases at increased sensitivity.

Calculations. The spectra obtained were analyzed by the usual mass spectrometric analytical methods. The calculations of the composition were made as follows: letting μ_I, μ_M, μ_A, μ_B, etc., be the microns of pressure observed for the internal standard gas, *I*, main component, *M*, and impurity gases, *A*, *B*, etc., respectively, from run 1 and the calibration runs, the mole ratio of internal standard to main component, $R_{I/M}$, is calculated.

$$\frac{\mu_I}{\mu_M} = R_{I/M} \tag{1}$$

From run 2, and the calibration runs:

$$\frac{\mu_A}{\mu_I} = R_{A/I}; \quad \frac{\mu_B}{\mu_I} = R_{B/I}; \text{ etc.} \tag{2}$$

where $R_{A/I}$, $R_{B/I}$, etc., are the mole ratios of impurity gases to the internal standard. Combining these mole ratios, the mole ratio of each impurity to the main component is calculated.

$$R_{I/M} \times R_{A/I} = R_{A/M}; \text{ etc.} \tag{3}$$

Table I. Noncondensable Impurities in Condensable Gases

	Mole %		
	Added	Found	Δ
Mixture I			
CO_2 (by difference)	99.66	99.67	.....
Air	0.127	0.129	+0.002
CO	0.208	0.197	−0.011
Ne—internal standard			
Mixture II			
Propane (by difference)	99.74	99.74	.....
He	0.112	0.114	+0.002
H_2	0.112	0.117	+0.005
O_2	0.034	0.032	−0.002
Ne—internal standard			
Mixture III			
CO_2 (by difference)	99.45	99.46	.....
O_2	0.111	0.109	−0.002
N_2	0.222	0.222	0.000
CO	0.215	0.205	−0.010
Ne—internal standard			
Mixture IV			
SO_2 (by difference)	99.46	99.50	.....
O_2	0.036	0.034	−0.002
N_2	0.037	0.045	+0.008
CO	0.116	0.102	−0.014
H_2	0.205	0.198	−0.007
CH_4	0.114	0.086	−0.028
A	0.035	0.034	−0.001
Ne—internal standard			

	Analysis, %	
	I	II
Mixture V (unknown)		
CO_2 (by difference)	99.847	99.842
CO	0.102	0.102
O_2	0.017	0.018
N_2	0.034	0.038
Ne—internal standard		

Table II. Condensable Impurities in Noncondensable Gases

	Mole %		
	Added	Found	Δ
Mixture I			
Dry CO_2 free air (by difference)	99.62	99.66	.....
Ethanol	0.087	0.072	−0.015
Acetone	0.032	0.028	−0.004
Ethyl ether	0.048	0.043	−0.005
n-Pentane	0.084	0.074	−0.010
Ethyl bromide	0.130	0.125	−0.005
SO_2—internal standard			

From the mole ratios of impurity to main component the molar composition is calculated by simple algebraic methods.

$$\text{Mole \% } A = 100 \frac{R_{A/M}}{(1 + R_{A/M} + R_{B/M} + \dots)} \quad (4)$$

$$\text{Mole \% } M = 100 \frac{1}{(1 + R_{A/M} + R_{B/M} + \dots)}$$

By this method one does not independently calculate the main component percentage but only the difference between the percentages of impurities and 100%, the same result being achieved by direct subtraction.

BLANK. In each case cited here except the unknown Mixture V, Table I, a blank was run on the pure main component gas using the identical procedure. In a few cases 1 or 2 parts per 100,000 of impurities were found. These amounts were subtracted from the total in calculating the percentages found in the mixtures shown in Table I.

RESULTS

The results on several synthetic mixtures are shown in Tables I and II.

The accuracy of the method for noncondensable impurities in the range of 30 to 200 parts per 100,000 is within 5%, based on the impurity added, except for carbon monoxide, which seems to be uniformly low by about 10 parts per 100,000, and methane in sulfur dioxide (Mixture IV), which is low by about 25%. In mixtures of carbon monoxide and nitrogen, the analyses were made for these components by removing all other components from the spectra and adjusting the respective contributions of carbon monoxide and nitrogen to the 12, 14, 16, and 28 peaks to give the best fit to the residual spectrum on all these peaks. The spectrometer used shows a background at masses 12, 16, and 28, which is believed due to carbon monoxide produced on the filament, and the amount of this background varies with the composition of gas being run. The existence of this background makes an absolute carbon monoxide–nitrogen split difficult, although the split on any given sample of gas is reproducible. In the case of methane in sulfur dioxide, the use of neon as an internal standard for methane and use of liquid nitrogen separation is probably not a justifiable procedure considering the relative vapor pressures of neon and methane at this temperature. Assuming Henry's law can be applied under these conditions, the mole fraction of solute being very low and there being no obvious interactions (*5*), methane would have an ideal solubility about 16 times as great in sulfur dioxide as oxygen, about 20 times as great as argon, about 40 times as great as carbon monoxide, and about 76 times as great as nitrogen, if all were present at the same partial pressure, while hydrogen and neon would have negligible solubilities by comparison. For samples containing methane impurities the use of a higher condensation temperature and different internal standard should produce better results.

The absolute accuracy of condensable impurities in air is about the same as that of noncondensable impurities, as is shown in Table II. In this example results for all the condensable impurities are a few per cent low. This is probably due to adsorption on the glass disk and walls of the mixing chamber in the case of oxygenated impurities, and absorption in stopcock grease in the case of pentane and ethyl bromide, resulting in the actual composition being lower than that calculated from the dipper volumes.

APPLICABILITY OF METHOD

The method is applicable in principle to the determination of much lower concentrations of impurities than those used in the experiments here. In practice the method will be limited by the linear range of the spectrometer used; the sensitivity ratios of the internal standard and gas components; the amount of sample available or which can be handled; and differential solubility effects of the internal standard and impurities in the condensed phase, which will become more pronounced and may lead to serious errors in the determination of very small amounts of noncondensable impurities. No attempt was made to extend the method to the range of parts per million when it was found difficult to prepare samples of condensable gases free of noncondensable impurities to much better than one part per hundred thousand. Therefore, no lower limit on the applicability of the method can be set from the experiments reported here.

The extension of the method to other condensation temperatures and the use of other internal standards is obvious. The main component need not be a pure gas but can be any mixture which can be analyzed by ordinary methods either on the total gas run with the internal standard or in a separate run using the original gas mixture. Thus in Mixture I, Table II, the results could have been reported in terms of oxygen, nitrogen, and argon contents plus the condensable impurities just as well as in terms of air and the impurities. In certain cases, as suggested by Hindin and Grosse (*6*), it might be convenient to add two internal standards to cover impurities in different concentration ranges or use two standards and two condensation temperatures to achieve the maximum sensitivity on components differing widely in properties. Each case encountered must be considered separately, and the procedure adapted to fit the needs of the mixture under consideration.

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Separations with a Micro Mercury Cathode

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THE conventional mercury cathode (*2*, *4*) used for separations of metals is not very satisfactory with small volumes of solution, because the surface of the mercury in contact with the solution is limited. Keeping the solution thoroughly stirred and avoiding spray losses are difficult in electrolyzing small volumes.

These difficulties can be eliminated by using a rigid metal cathode plated with liquid mercury. The mercury surface is thus increased twofold, as both surfaces of the electrode are in contact with the solution, and stirring is accomplished by the evolution of gases during electrolysis. A rigid mercury cathode of brass wire mesh coated with mercury was first used by Pawcek (*5*). A more detailed investigation was made later by Boettger (*1*). These investigators used large electrodes and were interested primarily in weighing the deposited metals, rather than in separations.

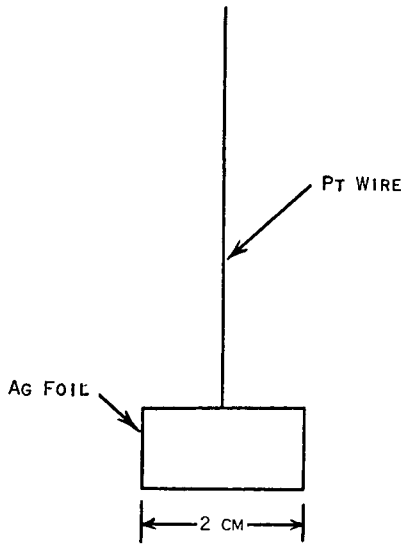


Figure 1. Construction of Cathode

In the author's investigations an electrode of silver foil 1.5 × 2 cm., coated with mercury, was used.

CONSTRUCTION OF ELECTROLYSIS CELL

Preparation of Electrode. The cathode is constructed as shown in Figure 1.

A 5-mil silver foil is used, spot-welded to a platinum wire. The foil is cleaned by rubbing with fine-gage steel wool, then bent into a semicircular shape and immersed in 6 *N* nitric acid for a minute or two to clean the surface further. Mercury is applied to the surface of the electrode by electrolysis of a 10% solution of mercurous nitrate containing a few drops of nitric acid. Electrolysis is continued until the surface of the silver foil is completely covered with liquid mercury and a noticeable deposit of liquid mercury hangs on the bottom of the electrode. The electrode is then removed from the mercurous nitrate solution and washed with water. The electrode is conditioned by placing it in a dilute sulfuric acid solution and electrolyzing at a current of 1 ampere for about 15 minutes. It is then ready for use.

Procedure. A 3- to 5-ml. volume of the solution to be analyzed (0.5 to 1.0 *N* in sulfuric acid and free from other anions) is placed in the electrolytic cell, a flat-bottomed tube of dimensions shown in Figure 2.

The prepared cathode is introduced to the bottom of this tube. A platinum wire, approximately 12-gage, serves as the anode. The mercury-coated cathode should be completely immersed in the solution; otherwise mercury will dissolve at the liquid-air interface. The cell is suspended in a water bath at room temperature to effect cooling during the electrolysis. The solution is electrolyzed 1 hour, the current being 1 ampere during the first 45 minutes and 0.5 ampere during the last 15 minutes. Higher current will cause mercury to be lost from the cathode. The sides of the cell should be washed down at 15-minute intervals with a small amount of water. At the end of 1 hour and with the current still on, the cathode is lifted from the solution and washed immediately with a small amount of water, the washings going into the electrolysis cell. The solution remaining in the electrolysis cell is now ready for analysis.

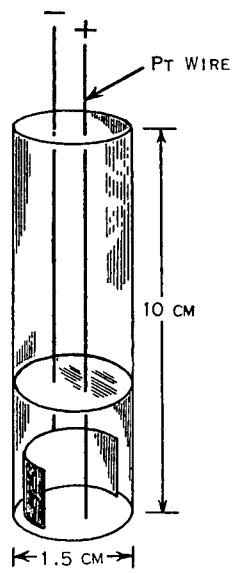


Figure 2. Electrolytic Cell

The efficiency of the cathode was tested by removing iron and/or copper from pure solutions of aluminum(III), uranium(VI), and zirconium(IV) ions (Table I).

These data indicate that the micro mercury cathode made separations as effectively as the conventional mercury cathode (*3*, *4*), the separable metal ions being completely removed as shown by colorimetric and radiochemical tests. Iron and copper were determined colorimetrically with 1,10-phenanthroline and diethyldithiocarbamate, respectively. The quantitative recovery of the remaining metal ions was shown by precipitation of the aluminum as the hy-

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Table I. Separations Effected with a Micromercury Cathode

(Sample volume 3 to 5 ml.)

	Separable Metals			Nonseparable Metals		
Sample	Identity	Added, mg.	Found, mg.	Identity	Added, mg.	Found, mg.
1	Fe(III)	1	None	Al(III)	250	249
2	Cu(II)	10	None	Al(III)	100	100
3	Fe(III)	10	None	Al(III)	0.90	0.89
	Cu(II)	10	None			
4	Fe(III)	10	None	U(VI)	2.53	2.51
5	Cu(II)	10	0.005	U(VI)	2.53	2.55
6	Fe(III)	10	None	U(VI)	0.485	0.470
	Cu(II)	10	0.001			
7	Fe(III)	10	None	Zr(IV)	0.91	0.90
	Cu(II)	10	None			

droxide, and by potentiometric titration of the uranium with ceric sulfate. Zirconium was determined by precipitation as the phosphate.

DISCUSSION

Electrodes of copper, lead, and pure platinum were also used as bases for the mercury coating, but were not so satisfactory as the silver electrode described. The mercury did not adhere well to the platinum, and the lead and copper introduced these ions as impurities in the test solution. The stem of the electrode must be of an inert material, as the solution tends to attack the metal at the liquid-air interface.

The silver-mercury electrode prepared as described above holds about 0.3 to 0.5 gram of liquid mercury on its surface, and can remove about 25 mg. of iron from solution.

The silver foil base may be prepared for re-use by immersing the electrode in 1 to 2 *N* nitric acid, which slowly dissolves off the mercury coating but does not attack the silver to any great extent. The electrode is then treated as described. If only a few milligrams of impurity were deposited on the electrode surface, the same electrode may be re-used after simple immersion in dilute (2 to 4 *N*) sulfuric acid.

ACKNOWLEDGMENT

The author wishes to thank H. H. Willard for suggesting this investigation and for the helpful advice given.

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Determination of Schiff Bases by Titration in Nonaqueous Solutions

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ALTHOUGH numerous papers in the recent literature are concerned with the titration of organic bases in nonaqueous solutions (*4–7, 9–12*), none of these deals specifically with the determination of Schiff bases. Wagner, Brown, and Peters (*17*) were the first to use salicylaldehyde in differentiating between primary and secondary amines, and Siggia, Hanna, and Kervenski (*15*) later reported on this method.

When this work was nearing completion, an excellent article was published by Fritz (*5*) with regard to the use of acetonitrile as a solvent to differentiate quantitatively between amines of various base strengths. The titration of aliphatic-aromatic amine mixtures resulted in two distinct breaks in the curve for each amine present in the combination.

The method described in this paper shows that Schiff bases can be conveniently analyzed by nonaqueous titration, and, in addition, impurities present in the form of the parent amines can be determined in this manner.

APPARATUS

Beckman pH meter (Model G) or similar titrator.
Glass electrode, Beckman Catalog No. 1190-42.
Calomel electrode, Beckman Catalog No. 1170.

REAGENTS

Acetic acid, reagent grade, glacial.
Acetic anhydride, reagent grade, 90 to 95%.
Acetonitrile, Eastern Chemical Co. or equivalent.
p-Dioxane, Carbide and Carbon Chemicals Co. or equivalent.
Methyl violet, 0.1% solution in glacial acetic acid.
Perchloric acid in acetic acid. Dissolve 8.5 ml. of 72% perchloric acid in 100 ml. of glacial acetic acid, add 22 ml. of acetic anhydride, and let stand overnight. Dilute to 1 liter with glacial acetic acid.
Perchloric acid in *p*-dioxane (0.01 *N*). Dissolve 0.85 ml. of 72% perchloric acid in 1 liter of *p*-dioxane.
Perchloric acid in *p*-dioxane (0.1 *N*). Dissolve 8.5 ml. of 72% perchloric acid in 1 liter of *p*-dioxane.
Potassium acid phthalate, primary standard grade.

PREPARATION OF SCHIFF BASES

All but two of the compounds listed in Table I have been previously reported. *N*-Benzylidine-*n*-hexylamine (133° at 8 mm.) and *N*-*p*-chlorobenzylidine-*n*-hexylamine (147° at 6 mm.) are prepared by reaction of equimolar proportions of amine and aldehyde in ethyl alcohol containing anhydrous potassium carbonate. The solutions are filtered after remaining at room temperature for 48 hours, the alcohol is removed with the aid of a water pump, and the Schiff bases are distilled under vacuum.

Procedure A. Dissolve the sample containing 3 meq. (accurately weighed) of Schiff base in 50 ml. of acetic acid. Titrate

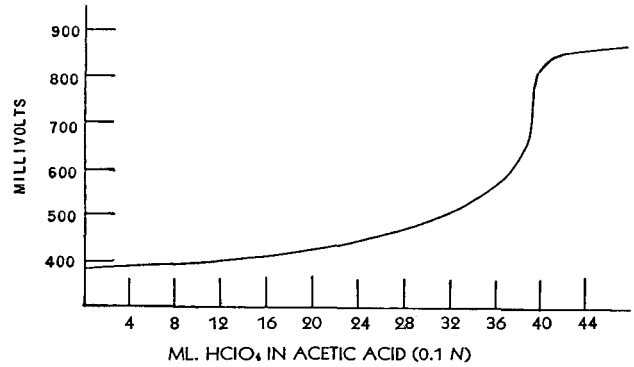


Figure 1. Titration of 1 to 1 Mixture of Aniline and *N*-Benzylidineaniline in Acetic Acid

Table I. Analytical Results on Schiff Bases by Three Different Methods

Schiff Base	Ref.	Procedure A, %	Nitrogen, %	2,4-Dinitrophenylhydrazone, %
N-*n*-Butylidine-*n*-butylamine	(*3*)	99.6	99.6	.....
N-Benzylidine-*n*-butylamine	(*16*)	99.5	99.6	100.0
N-Benzylidine-*n*-hexylamine	..	99.4	99.4	100.2
N-*p*-Chlorobenzylidine-*n*-hexylamine	..	100.0	99.9	100.9
N-*p*-Methoxybenzylidinebenzylamine	(*14*)	98.9	98.9	99.8
N-*p*-Methoxychlorobenzylidinebenzylamine	(*13*)	99.4	99.5	100.1
N-Benzylidineaniline	(*1*)	99.7	99.8	100.2
N-*n*-Butylidineaniline	(*6*)	99.0	99.1	.....
1,2-Bis(benzylidineamino)-ethane	(*8*)	99.7	99.8	100.1
N^4-*p*-Methoxybenzylidinesulfathiazole	(*2*)	97.8	97.6	98.3

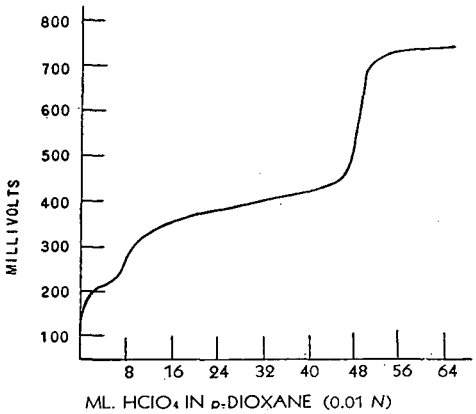


Figure 2. Titration of *N*-Benzylidine-*n*-hexylamine Containing 10% *n*-Hexylamine in Chloroform

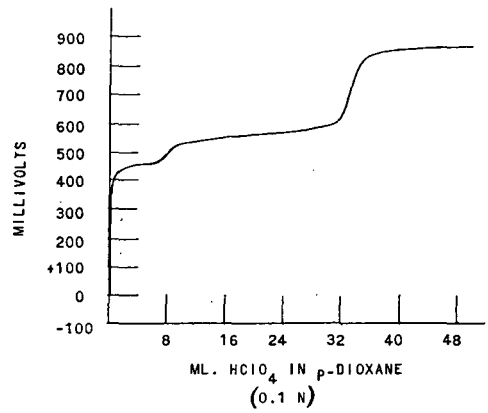


Figure 3. Titration of *N*-Benzylidineaniline Containing 10% Aniline in Acetonitrile

potentiometrically with 0.1 *N* perchloric acid in acetic acid using the millivolt scale of the pH meter or methyl violet indicator to a blue-green end point.

Standardize the titrant in the usual manner (*7*).

Procedure B (*11*). Dissolve the sample containing approximately 0.3 meq. of total Schiff base and amine in 25 ml. of chloroform and titrate potentiometrically with 0.01 *N* perchloric acid in dioxane. Standardize the titrant against purified diphenylguanidine in chloroform, using the pH meter.

Procedure C (*5*). Dissolve the sample containing about 3 meq. of total Schiff base and amine in 50 ml. of acetonitrile and titrate potentiometrically with 0.1 *N* perchloric acid in dioxane. Run a 50-ml. blank on each batch of acetonitrile.

With the exception of N^4-*p*-methoxybenzylidinesulfathiazole, the potential change at the equivalence point using Procedure A was so great (70 to 100 mv. per 0.1 ml. of volumetric solution) that no record of the potential change was necessary. In the case of the sulfathiazole Schiff base, the potential change was on the order of 10 to 15 mv. per 0.1 ml. of titrant, and its exact determination required recording to note its position. However, when Procedure C was employed for this substance, a much greater break in the titration curve occurred, which obviated the need to plot points.

Precipitation of 2,4-Dinitrophenylhydrazones. To about 1 meq. (accurately weighed) of Schiff base in 50 ml. of ethyl alcohol is added 50% excess of a 1% solution of 2,4-dinitrophenylhydrazine in 2 *N* hydrochloric acid. The precipitate forms immediately and is allowed to remain overnight at room temperature. It is then filtered off, washed with 2 *N* hydrochloric acid, and dried to constant weight.

SCOPE

Ten Schiff bases were prepared and the analytical data compiled by titrimetric, nitrogen, and dinitrophenylhydrazone methods of analyses appear in Table I. Purity values obtained by the latter procedure vary between 0.4 and 0.9% higher than those of the other two methods. Shoppee (*14*) noted that the *p*-nitrophenylhydrazones of halogen and methoxy-substituted benzaldehydes appeared to occlude small amounts of impurities, and he reported analytical results on these classes of compounds between 100.5 and 104%. There is excellent agreement between the titrimetric and nitrogen assay methods. The results of assays using methyl violet indicator lie within 0.1% of those obtained potentiometrically (Procedure A).

No differentiation between Schiff bases and the parent aliphatic or aromatic amines could be accomplished by Procedure A (Figure 1). This is probably due to the leveling effect of acetic acid (*5*). Employing the technique of Pifer, Wollish, and Schmall (Procedure B) (*11*), aliphatic amines could be quantitatively distinguished from their respective Schiff bases (Figure 2). Only by the method of Fritz (Procedure C) (*5*) was it possible to effect a quantitative differentiation between aniline and *N*-benzylidineaniline (Figure 3). By means of Procedures B and C amine impurities occurring in Schiff bases in concentrations as low as 1% can be determined by simply increasing the sample size.

Only one inflection was observed in the titration curve of *N*-butylidineaniline when following the three procedures described above. This compound is reported to contain both an azomethine and secondary amine groupings (*6*). In addition, equimolar mixtures of aniline and *N*-butylidineaniline and sulfathiazole and N^4-*p*-methoxybenzylidinesulfathiazole yielded only one break in their titration curves. These results were duplicated when acetic acid was substituted for dioxane as solvent for the perchloric acid (*5*) using Procedure C.

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Polarographic Determination of Molybdenum in Presence of Tungsten

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No polarographic method for the determination of molybdenum in the presence of a large excess of tungsten has been described, and indeed few data on the polarographic characteristics of the two elements individually are available. To avoid loss of molybdenum by coprecipitation with hydrous tungstic oxide, which readily separates from noncomplexing solutions, and to avoid the necessity of a preliminary chemical separation, it is necessary to find a supporting electrolyte which not only can retain considerable amounts of tungsten(VI) in solution but also gives a well-developed molybdate wave at less negative potentials than the wave due to tungstate.

Data secured by Carritt (*2*) on the polarography of molybdenum(VI), and by Lingane and Small (*3*) on the polarography of tungsten(VI) in hydrochloric acid media indicate that these solutions fulfill the first of these desiderata but not the second. Therefore hydrochloric (and, presumably, other hydrohalic) acid solutions are useless for the present purpose.

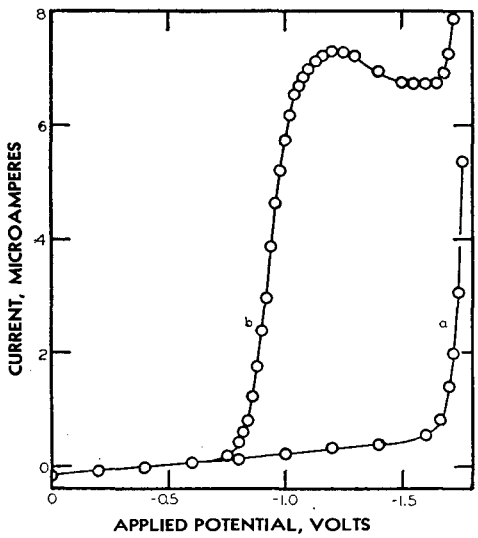


Figure 1. Polarogram of 1.00 *M* Sodium Citrate Solution

a. Titrated to pH 7.1 with perchloric acid
b. After addition of 0.93 m*M* sodium molybdate

It has been found, however, that in a 1 *M* sodium citrate buffer of pH 7 molybdenum(VI) gives a wave possessing a small maximum but an excellently defined plateau, and that tungsten(VI) neither precipitates nor gives an interfering reduction wave. Accordingly the properties of the molybdenum wave were investigated and a method for the determination of molybdenum in tungsten compounds has been developed.

EXPERIMENTAL

A stock solution of sodium molybdate was standardized by titration with potassium permanganate solution after passage through a Jones reductor into an air-free solution of excess ferric ammonium sulfate. The permanganate had been standardized against standard sample 40e of sodium oxalate supplied by the National Bureau of Standards. The standard error of the mean concentration of molybdenum in the stock solution was ±0.09%.

Polarographic measurements were usually made with a calibrated Sargent-Heyrovský Model XII polarograph, but the diffusion current constant data were secured with the manual polarograph previously described (*4*). All measurements were made with the cell immersed in a water thermostat at 25.00° ± 0.02° C. A Beckman Model G pH meter was used for the pH measurements.

All weights and volumetric apparatus were calibrated by conventional techniques. All chemicals were ordinary reagent grade.

DATA AND DISCUSSION

Figure 1 shows a typical polarogram of molybdenum(VI) in 1 *M* sodium citrate, pH 7. The half-wave potential in this medium is −0.927 ± 0.002 volt (all potentials are referred to the saturated calomel electrode), and the slope of the wave ($E_{3/4} - E_{1/4}$ = −96 mv.) shows that the reduction is thermodynamically irreversible. In 0.1 *M* sodium citrate at the same pH, $E_{1/2}$ = −1.111 ± 0.003 volts and $E_{3/4} - E_{1/4}$ = −112 mv. Although the plateau is better defined in the more dilute citrate solution, because the rounded maximum does not appear, it is not attained until a potential at which reduction of tungsten(VI) begins (Figure 2). Curiously, although increasing the citrate concentration facilitates the reduction of molybdenum, it has the opposite effect on the tungsten wave: The residual current in 1 *M* citrate appears to be not at all affected by the addition of even 0.2 *M* tungstate. The shape of the molybdate wave in the 1 *M* citrate buffer is not affected by variations in pH between at least 6 and 8, although the half-wave potential becomes somewhat less negative with decreasing pH.

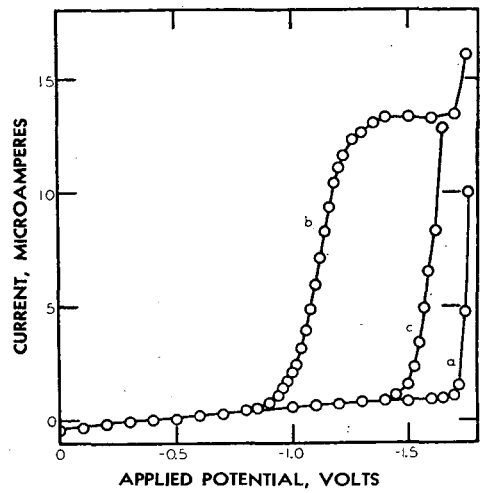


Figure 2. Polarogram of 0.10 *M* Sodium Citrate Solution

a. Titrated to pH 7.0 with perchloric acid
b. With 1.64 m*M* sodium molybdate added
c. With 1.62 m*M* sodium tungstate

If molybdenum is assumed to be present in these solutions as MoO_4^{--}, and if the diffusion coefficient of this ion is assumed to be equal to that of chromate ion (1.07×10^{-5} sq. cm. per second), the diffusion current constant data reported below give a value for n of about 1.9, indicating that the reduction proceeds to the +4 state. In agreement with this conclusion, a millicoulometric electrolysis (*1*) showed that in this medium the reduction of 0.2725 micromole of molybdenum(VI) requires 0.5468 microfaraday, whence n = 2.007. Furthermore, an amperometric titration of molybdenum(VI) with standard vanadium(II) perchlorate solution showed that 1.997 ± 0.006 moles of vanadium(II) were required to reduce 1 mole of molybdenum. This is the first reported reduction of molybdenum(VI) to the +4 state at

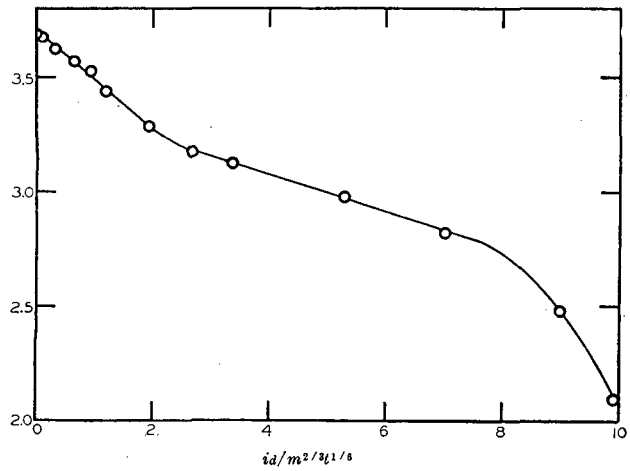


Figure 3. Plot of I vs. $i_d/m^{2/3}t^{1/6}$ for Molybdenum(VI) in 1.0 M Sodium Citrate, pH 7

the dropping electrode. Apparently molybdenum(IV) forms a fairly stable citrate complex, which would explain the shift of the half-wave potential to more positive values with increasing citrate concentration.

Table I shows data on the diffusion current constant of molybdenum(VI) in the 1 M citrate buffer. It is evident that $i_d/Cm^{2/3}t^{1/6}$ decreases continuously with increasing molybdenum concentration. Such a phenomenon is usually due either to improper correction for the residual current or to the occurrence of a stirring effect in the layer of solution immediately surrounding the drop. The first of these generally follows from attempts to determine the residual current by extrapolation of the portion of the current-voltage curve preceding the wave, and may be dismissed in the present case. The other possibility, if true, would predict that the diffusion current would become more nearly proportional to the molybdenum concentration if the drop time were greatly increased or if a maximum suppressor were added. Some measurements were made with a capillary whose drop time at −1.6 volts was 7.3 seconds: The diffusion current constants at equal molybdenum concentrations agreed very closely with those given in Table I. Furthermore, neither gelatin nor Triton X-100 significantly altered the magnitude or direction of the change, though both gave diffusion current constants slightly and uniformly lower than those secured in their absence. Such stirring effects tend to decrease, and finally disappear, as the concentration of reducible ion is increased, but these data show no tendency to approach constancy at high molybdenum concentrations. The effect is doubtless due to an increasing degree of polymerization of the predominating molybdate species with increasing concentration, resulting in a decrease in the effective value of the diffusion coefficient.

Because of this behavior, C cannot be calculated directly from data on i_d, m, and t. The simplest treatment involves constructing a large scale plot of $i_d/m^{2/3}t^{1/6}$ vs. C from the data of Table I, and using this to convert the experimental data into the corresponding values of C. It is somewhat more accurate, especially at low values of C, to construct a plot of I vs. $i_d/m^{2/3}t^{1/6}$ (Figure 3): from this the appropriate value of I can easily be read off to well within the probable error of the data. The latter procedure is the one followed in the remainder of this work.

Table I. Diffusion Current Constant of Molybdenum(VI) in 1 M Sodium Citrate, pH 7.1

Known volumes of 10.43 and 104.3 mM sodium molybdate solutions were added to a known volume of 1.00 M sodium citrate previously titrated to pH 7.09 with perchloric acid. $E_{d.e.}$ = −1.60 volts vs. S.C.E., t = 1.737 seconds, $m^{2/3}t^{1/6}$ = 2.3006 mg.$^{2/3}$ sec.$^{-1/2}$ Diffusion currents corrected for residual current (0.885 μa.)

[Mo(VI)], mM	i_d, μa.	$i_d/Cm^{2/3}t^{1/6}$
0.0252	0.213	3.667
0.0893	0.744	3.621
0.1774	1.457	3.570
0.2641	2.142	3.526
0.3496	2.765	3.438
0.5912	4.466	3.284
0.8314	6.08	3.180
1.071	7.725	3.135
1.783	12.21	2.977
2.485	16.15	2.826
3.628	(20.7)[a]	2.48
4.744	(22.9)[a]	2.10

[a] Galvanometer deflections were very erratic.

Table II. Determination of Molybdenum in Sodium Tungstate

Mo Added, Mg.	i_d, μa.	I	Mo Found, Mg.	Total Mo Present, Mg.
0	0.081, 0.077, 0.076, 0.086, 0.072, 0.084	3.678	0.045 ± 0.002	(0.045)
0.050	0.173, 0.161, 0.168, 0.162	3.672	0.094 ± 0.003	0.095
0.100	0.257, 0.250, 0.254	3.665	0.145 ± 0.001	0.145
0.150	0.340, 0.350	3.658	0.197 ± 0.003	0.195
0.200	0.415, 0.435, 0.427	3.650	0.243 ± 0.004	0.245
0.300	0.609, 0.585, 0.607	3.633	0.345 ± 0.006	0.345
0.400	0.765, 0.795, 0.770	3.617	0.448 ± 0.008	0.445
0.800	1.45, 1.42, 1.49, 1.40	3.558	0.84 ± 0.02	0.845
2.00	3.30, 3.40, 3.36, 3.34	3.391	2.06 ± 0.02	2.04
10.0	13.7, 13.9, 13.9	2.918	9.88 ± 0.07	10.04

It may be illustrated by the following data, secured in the analysis of a sample of reagent grade sodium tungstate dihydrate, whose molybdenum content was given by the manufacturer as 0.002%.

A 30.15-ml. portion of 1 M sodium citrate, pH 7, was placed in an H-cell and deaerated, and the residual current at −1.6 volts was read from the visual scale of the polarograph. Then 1.00 gram of the sample was added and, when solution was complete, the current at −1.60 volts was remeasured. The diffusion current of the molybdenum was 0.068 μa.; since $m^{2/3}t^{1/6}$ was 2.301 mg.$^{2/3}$ sec.$^{-1/2}$, $i_d/m^{2/3}t^{1/6}$ was 0.029. From Figure 3 the corresponding value of I is 3.683, whence C = 0.029/3.683 = 0.0080 millimolar. Accordingly, the sample contained (0.0080)(95.95)(30.15) = 23γ of molybdenum, corresponding to 0.0023% of the sample weight. The entire analysis consumed approximately 12 minutes.

The reliability of the method is shown by the data in Table II. In each of these analyses a 2.00-gram portion of sodium tungstate containing 0.0023% molybdenum was weighed into a 50-ml. volumetric flask, a known volume of standard sodium molybdate solution was added, and the solution was diluted to the mark with the citrate buffer and analyzed by measuring its diffusion current at −1.60 volts. The value of $m^{2/3}t^{1/6}$ for the capillary used was 2.301 mg.$^{2/3}$ sec.$^{-1/2}$, and the residual current was found in a separate experiment to be 0.885 μa. The mean error in the determination of 0.05 to 10 mg. of molybdenum in the presence of 1.1 grams of tungsten corresponds to about ±2% of the amount of molybdenum present.

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Separation of Cerium from the Rare Earths by Precipitation as Iodate from Homogeneous Solution

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THE separation of cerium by precipitation as ceric iodate was originated by Brinton and James (*1*). Excess of potassium iodate was added to the cerium(IV) solution containing nitric acid. The precipitate was bulky and gelatinous, with a great tendency to adsorb impurities. It was difficult to filter and wash and could not be ignited directly to the oxide for final weighing. Chernikhov and Uspenskaya (*2*) precipitated cerium as $2Ce(IO_3)_4.KIO_3.8H_2O$ from a solution containing a little nitric acid and 5% potassium iodate.

The present work was undertaken to obtain a dense, crystalline precipitate of ceric iodate by precipitation from homogeneous solution according to the methods developed by Willard (*3*) and coworkers. Such a precipitate would furnish a better separation from the rare earths. Two possible methods are: (1) oxidation of iodine to iodate in the presence of cerium(IV) and (2) oxidation of cerium(III) to cerium(IV) in the presence of excess of iodate, cerous iodate being soluble.

Iodine can be conveniently oxidized to iodic acid by chlorate, bromate, or persulfate. The reaction with chlorate was too slow and precipitation of cerium was incomplete. With bromate, complete precipitation of cerium was occasionally obtained, but the results were erratic. With persulfate complete oxidation occurred only when the concentration of nitric acid was much below 0.1 *M* and even then the reaction was very slow. Periodic acid precipitated cerium incompletely.

Cerium(III) was satisfactorily oxidized to cerium(IV) by either bromate or persulfate and the use of both these reagents was investigated in detail.

REAGENTS

Ammonium Hexanitratocerate. This was reagent grade from the G. Frederick Smith Chemical Co. and when analyzed by direct ignition or by oxalate precipitation was found to have the theoretical composition of 31.39% CeO_2. The salt was dried at 80° C. for 1 hour.

Ammonium Iodate. This was prepared by neutralizing reagent quality iodic acid with freshly filtered, concentrated ammonia solution and evaporating at about 50° C.

Ammonium Persulfate and Sodium Bromate were of analytical reagent quality. Potassium bromate is not so suitable because of the tendency of ceric iodate to carry potassium salts.

Salts of Rare Earth Metals. Oxides of lanthanum, neodymium, praseodymium, and samarium of 99% purity were from Research Chemicals, Inc. Gadolinium sulfate was from the Lindsay Chemical Co. Erbium and yttrium nitrates were from a German source and of unknown purity. They were all free from cerium and elements precipitated by iodate, and it was not necessary that they be entirely free from other rare earths.

CONDITIONS STUDIED

The various factors which influence the precipitation of ceric iodate were studied:

1. Concentration of nitric acid
2. Temperature
3. Concentration of ammonium iodate
4. Concentration of bromate or persulfate
5. Volume of solution
6. Stirring
7. Wash solution

EXPERIMENTAL

In all this work the precipitate was ignited to ceric oxide. This was brownish in color and the results were slightly high. The cause of this is unknown, but this error was completely eliminated by adding a drop or two of concentrated sulfuric acid to the precipitate and, after careful evaporation, igniting again at 800° to 900° C.

Concentration of Nitric Acid. In the oxidation by bromate, acid is consumed, but in oxidation by persulfate, acid is liberated. Therefore the initial acid concentration at which the solubility of the precipitate becomes appreciable will be greater in the bromate than in the persulfate method. A high concentration of acid gives a better separation from the rare earths. Table I shows the effect of varying the acid concentration.

Table I. Influence of Concentration of Nitric Acid on Quantitative Precipitation of Ceric Iodate

(In each experiment 3 grams of ammonium iodate and 3 grams of ammonium persulfate or 2 grams of sodium bromate were added)

Oxidant	HNO_3, *M*	CeO_2 Taken, Mg.	CeO_2 Found, Mg.	Error, Mg.
Persulfate	0.4	21.4	21.3	−0.1
Bromate	0.4	18.6	18.6	0
Persulfate	0.5	26.3	26.2	−0.1
Bromate	0.5	22.2	22.3	+0.1
Persulfate	0.6	29.3	15.5	−13.8
Bromate	0.6	21.1	21.1	0
Persulfate	0.8	28.1	20.5	−7.6
Bromate	1.2	25.2	25.3	+0.1
Bromate	1.4	19.6	18.1	−1.5

Temperature. Conditions were as in Table I, except that the solution was 0.5 *M* in nitric acid in all cases. In the persulfate method 40° to 60° was the best starting temperature and the solution stood overnight at 70° to 80° C In the bromate method the best starting temperature was 60° to 80° C., and the solution stood at room temperature overnight. It is essential in all cases to allow the solution to cool to room temperature before filtering. Sudden cooling in an ice bath was less effective. Apparently there is a tendency toward supersaturation.

Concentration of Ammonium Iodate. With 4 grams of ammonium persulfate and 300 ml. of 0.5 *M* nitric acid the precipitation of 25 mg. of ceric oxide showed a loss of 2 to 4 mg. when 1 gram of ammonium iodate was added, of 1.2 mg. with 2 grams of iodate, and no loss with 3 to 5 grams of iodate.

Amount of Oxidizing Agent. The amount of ammonium persulfate required for complete precipitation was at least 3 grams, and more than 5 grams caused low results because of the sulfuric acid formed in the process. Moreover, too much persulfate furnished enough acid to produce hydrogen peroxide, and this reduced the ceric salt. The proper amount of sodium bromate was from 1 to 3 grams. Amounts as large as 5 to 7 grams gave high results and the precipitate contained sodium.

Volume of Solution. In the bromate method the volume was varied between 100 and 700 ml. without affecting the results, except that 3 grams of ammonium iodate and 5 grams of bromate were needed in the latter case. In the persulfate method slightly low results were obtained with a volume of 500 ml., when 5 grams of persulfate and 4 grams of iodate were added.

Stirring. A better precipitate was obtained if the solution was continuously agitated with a mechanical stirrer except when it was on the hot plate. The time for complete precipitation was then shortened to 3.5 hours. If continuous stirring is not feasible, the solution should be stirred at frequent intervals.

Wash Solution. In the persulfate method no nonvolatile material was introduced and ten washings with water or dilute iodic

Table II. Precipitation of Pure Cerium Solutions
(0.5 *M* nitric acid)

CeO_2 Taken, Mg.	CeO_2 Found, Mg.	Error, Mg.	Oxidizing Agent
2.5[a]	2.6	+0.1	Persulfate
22.4	22.4	0	Persulfate
64.2	64.2	0	Persulfate
110.3	110.2	−0.1	Persulfate
176.9	176.9	0	Persulfate
247.0[b]	247.0	0	Persulfate
2.6[a]	2.5	−0.1	Bromate
12.4	12.3	−0.1	Bromate
84.4	84.4	0	Bromate
113.4	113.4	0	Bromate
196.7[b]	196.6	−0.1	Bromate

[a] Total volume of solution, 100 ml.
[b] Total volume of solution, 500 ml.

acid showed no appreciable solubility effect. In the bromate method, however, a 1% solution of iodic acid was much better than ammonium iodate or water. About 15 washings were required to remove all sodium from the precipitate; otherwise a positive error of 0.5 to 0.8 mg. was present.

ANALYTICAL PROCEDURE

Ammonium Persulfate as Oxidizing Agent. Dissolve the sample in a 400-ml. beaker. If it contains elements other than the rare earths, separate the latter as oxalates by adding oxalic acid. Wash thoroughly, dry, and ignite to oxides. Dissolve the oxides in enough warm sulfuric acid (2 parts of acid to 1 of water) for complete solution. If the sample contains 25 to 100 mg. of ceric oxide, dilute it to 300 ml. or to a smaller or larger volume if very small or large amounts are present. Add 8 to 9 ml. of nitric acid, specific gravity 1.42, per 300 ml. of solution. The solution will then be 0.4 to 0.5 *M* in nitric acid. Add 2 to 10 drops of 3% hydrogen peroxide and let the solution stand for a few minutes to reduce all cerium(IV), but avoid a large excess. The yellow color of cerium(IV) should disappear. Boil gently to destroy the excess of peroxide, taking care to avoid bumping. Cool the solution to about 40° to 60° C. Add 3 grams of ammonium iodate and stir until dissolved. No precipitate should appear; otherwise, incomplete reduction is indicated and another drop or two of peroxide should be added and the solution again boiled.

Add about 1 gram of ammonium persulfate and stir for 1 or 2 minutes. Place the solution where it will attain a temperature of 70° to 80° C. After 1.5 or 2 hours add about 2 grams more persulfate and allow the solution to stand on the hot plate for 2 or 3 hours more, or overnight if convenient. Remove from the hot plate and apply mechanical stirring while it cools to room temperature. Rapid cooling is undesirable and tends to form a slight turbidity which is difficult to filter. If a mechanical stirrer is not available, stir vigorously for 1 or 2 minutes in every 15 minutes, or at least four or five times. Filter through No. 40 Whatman filter paper. Wash the precipitate three times by decantation and 15 times on the filter with 1% iodic acid solution. Burn off the paper and ignite the precipitate for 15 to 30 minutes at the full heat of a Méker burner or in a muffle at 800° to 900° C. The ceric oxide is stained with dark brownish particles. Cool it and add dropwise enough concentrated sulfuric acid to cover the precipitate. Evaporate carefully to avoid spattering until all the sulfuric acid is removed and ignite again for 15 to 30 minutes. Cool and weigh as ceric oxide, CeO_2.

If a second precipitation is required, pour the supernatant liquid from the first precipitate through a No. 40 Whatman filter paper and wash the precipitate several times by decantation with 1 to 2% iodic acid solution, leaving in the beaker as much precipitate as possible. Wash the filter paper five or ten times with the same solution. Add to the moist precipitate in the beaker the exact quantity of concentrated nitric acid required in the precipitation. Add 10 drops of 3% hydrogen peroxide and warm until the solution is clear. Dilute to 300 ml. and if there is evidence of incomplete reduction add 2 or 3 more drops of hydrogen peroxide. Proceed with the precipitation as before and filter through the same filter. Wash, ignite, and weigh the ceric oxide as previously described.

Sodium Bromate as Oxidizing Agent. Treat the sample in exactly the same manner up to the boiling of the reduced solution. Cool the solution to 60° to 80° C. Add 3 grams of ammonium iodate and stir until dissolved. No precipitate should appear. From the 1.5 to 2 grams of sodium bromate required, add less than half of it. Allow the solution to stand at room temperature, and apply mechanical stirring for 1 to 1.5 hours. Add the second portion of bromate and stir for at least another 30 minutes. Allow it to stand at room temperature or overnight if convenient. Filter and proceed as in the persulfate method.

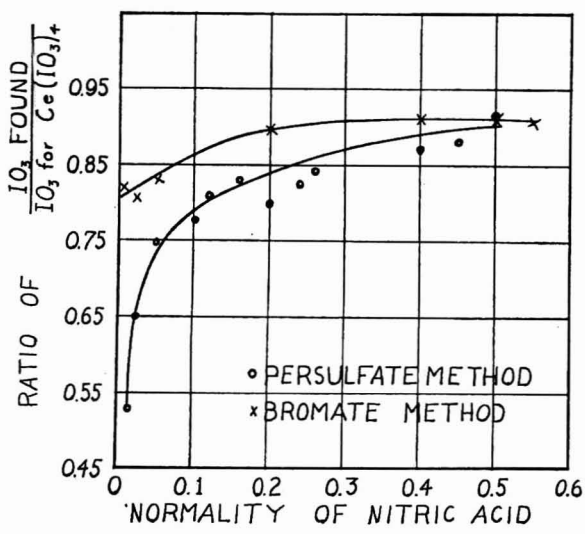


Figure 1. Influence of Acidity on Composition of Precipitate

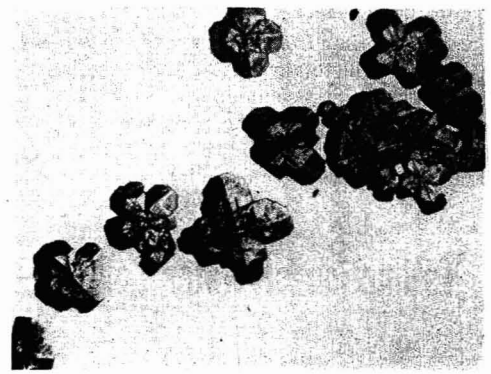


Figure 2. Photomicrograph of Ceric Iodate Crystals

Iodic acid may be used instead of ammonium iodate, but because this increases the acidity of the solution, the maximum concentration should then be 0.3 *M* nitric acid.

Table II shows the results obtained by the procedure described with pure cerium solutions.

Composition of Precipitate. Two samples of the same size were precipitated simultaneously in exactly the same manner at the desired acidity. One was ignited to ceric oxide and the other was treated with potassium iodide and a little acid. The iodine liberated was titrated with thiosulfate. This determined the amount of iodate in the precipitate and as the weight of cerium was known, the ratio of the weight of iodate found to the theoretical iodate for the known weight of cerium was calculated. If the precipitate were normal ceric iodate this ratio would be 1. It varied from 0.49 in 0.015 *M* nitric acid to 0.92 in 0.5 *M* acid. This is shown in Figure 1. At the highest acidity the formula for the precipitate, dried at 40° to 45° C. for 2 days, was approximately $Ce_2(IO_3)_7OH.xH_2O$, in which x varied from 3 to 7. A normal ceric iodate could doubtless be prepared in a much more concentrated nitric acid solution, in which it is soluble.

Figure 2 shows a photomicrograph of the crystals (kindly furnished by E. Staritzky, Los Alamos Scientific Laboratory). They are isomorphous with plutonium iodate.

Table III. Separation of Cerium from Individual Rare Earths

(300 ml. of 0.5 *M* nitric acid)

Earth Oxide Present, Mg.	CeO_2 Taken, Mg.	CeO_2 Found, Mg.	Error, Mg.	No. of Pptions.	Oxidizing Agent
30 Y_2O_3	22.2	22.2	0	1	Persulfate
30 Y_2O_3	26.6	27.0	+0.4	1	Bromate
30 Y_2O_3	22.2	22.3	+0.1	2	Bromate
24 La_2O_3	5.6	5.5	−0.1	1	Persulfate
48 La_2O_3	28.3	30.1	+1.8	1	Persulfate
60 La_2O_3	23.6	23.8	+0.2	2	Persulfate
24 La_2O_3	22.9	23.6	+0.7	2	Bromate
24 Pr_2O_3	25.1	25.3	+0.2	2	Persulfate
12 Pr_2O_3	3.9	4.0	+0.1	1	Persulfate
24 Pr_2O_3	26.1	27.1	+1.0	2	Bromate
41 Nd_2O_3	25.6	25.5	−0.1	2	Persulfate
82 Nd_2O_3	31.7	31.9	+0.2	2	Persulfate
41 Nd_2O_3	45.9	48.5	+2.6	1	Bromate
41 Nd_2O_3[a]	59.7	59.7	0	1	Bromate
30 Sm_2O_3	22.3	22.3	0	2	Persulfate
30 Sm_2O_3	25.4	25.3	−0.1	2	Bromate
15 Gd_2O_3	20.7	20.8	+0.1	2	Persulfate
30 Gd_2O_3	24.9	25.3	+0.4	2	Persulfate
30 Gd_2O_3	25.3	25.3	0	2	Bromate
30 Er_2O_3	21.3	21.2	−0.1	2	Persulfate
30 Er_2O_3	20.8	20.7	−0.1	2	Bromate

[a] 500 ml. volume.

SEPARATION OF CERIUM FROM OTHER RARE EARTH ELEMENTS

Known amounts of cerium were added to known amounts of rare earth salts and the procedure was carried out in the usual manner. The results of the separation from individual rare earths are shown in Table III.

The separation of cerium from a mixture of seven rare earths is shown in Table IV. The total weight of the oxides is seven times the weight shown in the first column.

It is obvious that in general the persulfate method gives a better separation than bromate and that in general the presence of up to 30 mg. of any rare earth oxide introduces no appreciable error in the persulfate method if two precipitations are made. If the volume is increased to 500 ml., considerably larger amounts can be tolerated.

Interfering Elements. The following ions gave no precipitate under the conditions recommended: magnesium, aluminum, cobaltous, nickelous, chromium, and molybdate. The following gave precipitates immediately: strontium, barium, bismuth, stannic, lead, silver, mercurous, mercuric, titanyl, uranyl, and thorium, and on standing manganese, ferric, zinc, cadmium, calcium, cupric, gallium, and indium precipitated at room temperature.

Ceric oxide obtained in this way can, of course, be determined titrimetrically by the use of a standard reducing agent.

Table IV. Separation of Cerium from a Mixture of Yttrium, Lanthanum, Praseodymium, Neodymium, Samarium, Gadolinium, and Erbium

(300 ml. of 0.5 *M* nitric acid, two precipitations)

Each Oxide, Mg.	CeO_2 Taken, Mg.	CeO_2 Found, Mg.	Error, Mg.	Oxidizing Agent
5	22.9	22.9	0	Persulfate
15	32.5	32.4	−0.1	Persulfate
30	26.8	26.9	+0.1	Persulfate
15	22.1	22.6	+0.5	Bromate

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Estimation of Water Content of Small Amounts of Proteinaceous Material

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IT IS often necessary to estimate the quantity of moisture present in 5- to 50-mg. samples of lyophilized proteinaceous materials such as pituitary hormones. The most widely used chemical methods for the determination of water employ the Karl Fischer reagent, but existing methods, in general, are not applicable to small samples. A convenient colorimetric procedure has been developed which employs the Fischer reagent.

Table I. Analytical Data for Sample of Lyophilized Pituitary Gonadotropic Hormone Preparation

	Mg.	Instrument Reading (Absorbance)
Water in standard	0	1.50
	0.200	0.83
	0.300	0.23
Protein	15	0.48
Calculated water content	0.26	

METHOD

The reaction is carried out in a dry box or under ordinary conditions on a day with low humidity. All glassware is separately wrapped in brown wrapping paper and dried at 110° C. for 2 hours.

Preparation of Reagent. Diluted Fischer reagent is prepared by adding the concentrated reagent to anhydrous methanol until a yellow color develops. The quantity of Fischer reagent to be added is arrived at empirically according to the following scheme: Ten milliliters of the diluted solution is put into a standard Coleman cuvette and 0.02 ml. of anhydrous methanol is added, using a Sahli hemoglobin pipet with a rubber tube and a mouthpiece. The methanol is not blown in with the breath, but rather by compression of the rubber tube. The pipet is then used as a stirring rod. To a similar tube 1 drop of water is added to produce decoloration; this is used for the blank setting of the Coleman Junior spectrophotometer. Measurement is made at 500 mμ. The contents of the first tube should have an absorbance of 2.0 if approximately 0.4 mg. of water is expected to be present, 1.5 for 0.3 mg., and 1.0 for 0.2 mg. or less. The diluted reagent is useful for several days if kept in a dry atmosphere.

Preparation of Standard Curve. Solutions of water in absolute methanol are prepared so that 0.100, 0.200, and 0.300 mg. are present in 0.02 ml. of solution. If greater accuracy is desired, intermediary standards should be prepared. Each standard is introduced into the diluted Fischer reagent and readings are made as indicated above.

Procedure. The cap is removed from the bottle containing the lyophilized material, 10 ml. of the diluted reagent is added, the bottle is stoppered, and its contents are mixed by swirling, care being taken that the solution does not come in contact with the stopper. The bottle is quickly centrifuged, the supernatant solution is transferred to a colorimeter tube, and a reading is taken, using a water-decolorized solution as a blank. The nonaqueous reactants may be determined on a heat-dried sample.

In Table I analytical data are shown. The complete determination takes less than 10 minutes.

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1-Fluoro-2,4-dinitrobenzene as a Quantitative Reagent for Primary and Secondary Amines

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SANGER (*6*) introduced 1-fluoro-2,4-dinitrobenzene as a quantitative reagent for labeling the free amino groups of proteins and peptides. Subsequently he and others have used this reagent for the identification and quantitative determination of free amino acids. The quantitative determination of histamine by means of 1-fluoro-2,4-dinitrobenzene was reported in previous publications from this laboratory (*4, 5*). The method described for histamine may be used for the determination of any diamine with one tertiary and one primary or secondary amino group capable of reacting with 1-fluoro-2,4-dinitrobenzene.

The purpose of this paper is to point out that 1-fluoro-2,4-dinitrobenzene has potentially an extensive usefulness as a quantitative reagent for primary and secondary amines, and to present a method which was designed for the quantitative determination of *d*-desoxyephedrine and which, perhaps with slight modifications for special cases, appears suitable for the determination of a number of primary and secondary amines. This method consists of reacting the amine with 1-fluoro-2,4-dinitrobenzene, converting the excess reagent to 2,4-dinitrophenol, separating the 2,4-dinitrophenylamine from the sodium salt of 2,4-dinitrophenol, and measuring the quantity of the 2,4-dinitrophenylamine by means of its light absorption. The absorbance of the solution of the 2,4-dinitrophenylamine is a linear function of the quantity of amine present.

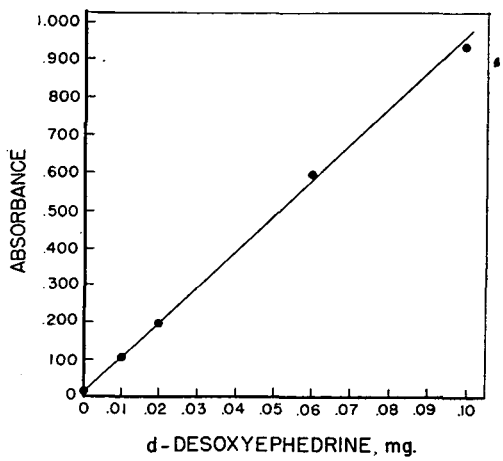


Figure 1. Relationship of Absorbance to Quantity of *d*-Desoxyephedrine in Original 0.1-Ml. Sample

Figure 1 shows the relationship between the absorbance of the final solution of the 2,4-dinitrophenyl derivative and the amount of *d*-desoxyephedrine originally used in the reaction. This relationship has been examined for several other amines as well—namely, diethyl-, di-*n*-butyl-, *n*-butyl-, *n*-hexyl-, benzyl-, and β-hydroxyethylamine. In every case a linear relationship was observed, with all points fitting closely to the line. As would be expected, the slope of the line differed from one amine to another.

The precision offered by this method is apparent from the data presented. The points shown in Figure 1 are averages of two sets of duplicates. The slope of the line calculated by the method of least squares is 0.940, with a standard deviation of 0.015. The authors were measuring 0.1-ml. samples of the various amine solutions with 1-ml. Mohr pipets drawn to a fine tip. If special micropipets were used, better precision should be expected. Even with the pipets used, the precision obtained compares very favorably with that of other colorimetric micromethods. It is doubtful that a 100% yield of any of the 2,4-dinitrophenylamines was obtained, but the yields were sufficiently reproducible under the specified conditions to afford a quantitative determination with satisfactory precision.

In an effort to learn the limitations of the proposed method, a number of primary and secondary amines were carried through the procedure described below, with the results shown in Table I. As the dinitrophenylamines were not isolated, their molar extinction coefficients, and hence the percentage yield for each derivative, are not known. For this reason, and because the amines used were stockroom samples without special purification, the significance of moderate differences in the absorbance values in Table I is unknown. It is clear, however, that the primary amines (even a very weak amine such as aniline) react readily with 1-fluoro-2,4-dinitrobenzene and that steric hindrance can block completely the reaction in the case of certain secondary amines—e.g., diisopropylamine and dicyclohexylamine. The very low reactivity of *N*-methylaniline is particularly interesting when compared to benzyl-*N*-ethylamine, benzyl-*N*-*n*-butylamine, dibenzylamine, and *d*-desoxyephedrine. Noteworthy is the fact that all the dinitrophenyl derivatives of the primary amines, except ethanolamine, have absorption maxima in the range of 325 to 335 mμ, while all the derivatives of the secondary amines, except dibenzylamine, have absorption maxima between 350 and 360 mμ. The dinitrophenyl derivatives of the primary amines, ethanolamine and histamine, both have absorption maxima in the same region as the secondary amine derivatives.

Table I. Absorbance of Solutions of 2,4-Dinitrophenyl Derivatives of Amines[a]

Amine	Absorbance[b]	Absorption Maximum, Mμ
Ethanolamine	0.409	350
Isopropylamine	0.520	330
n-Hexylamine	0.507	330
Aniline	0.361	335
Benzylamine	0.420	325–330
Dodecylamine	0.326	330
Diethylamine	0.584	355
Di-*n*-propylamine	0.525	355
Di-*n*-butylamine	0.402	355–360
Piperidine	0.423	355
2,3-Dimethylpiperidine	0.364	360
Benzyl-*N*-ethylamine	0.417	350
Benzyl-*N*-*n*-butylamine	0.339	350–355
Dibenzylamine	0.193	340–345
d-Desoxyephedrine	0.507	355
N-Methylaniline	0.066	355–360
Diisopropylamine	0.000	...
Dicyclohexylamine	0.000	...

[a] Concentration of amine derivative in each would be $3.5 \times 10^{-5} M$ if the yield were 100%.
[b] Averages from two to five pairs of replicates; most replicates were within ±5% of the average.

Though not to be preferred generally over some of the excellent methods now available for the determination of amines (*1, 3*), the method presented here appears to be advantageous for the determination of certain primary and secondary amines in the presence of tertiary amines, the determination of highly water-soluble amines such as ethanolamine, the qualitative identification as well as quantitative determination on the same sample.

REAGENTS

1-Fluoro-2,4-dinitrobenzene, prepared by the method of Cook and Saunders (*2*), 0.12 ml. dissolved in 10 ml. of absolute ethyl alcohol.

Sodium bicarbonate solution, 0.1*M*.

Sodium hydroxide, 0.2N in 60% dioxane.
Organic solvent, cyclohexane or s-tetrachloroethane.

PIPETS

For the best results, the aliquots of amine solution should be measured with micropipets. Reasonably good results can be obtained with 1-ml. Mohr pipets on which the tips have been drawn to a fine point.

PROCEDURE

Pipet carefully to the bottom of a 25-ml. glass-stoppered cylinder 0.1 ml. of aqueous amine solution containing 10 to 100γ of amine, 0.05 ml. of 1-fluoro-2,4-dinitrobenzene in alcohol, and 0.1 ml. of bicarbonate solution. Mix thoroughly and place the cylinder in a 60° water bath for 20 minutes. Add 0.4 ml. of 0.2N sodium hydroxide in dioxane and continue heating for 60 minutes. Dilute to 10 ml. with distilled water and extract with 10 ml. of cyclohexane. (In the case of ethanolamine and other highly water-soluble amines, extract with s-tetrachloroethane.) Separate the liquid layers and read the absorbance of the organic solvent at the wave length of maximum absorption as shown in Table I. Blanks on the reaction give an absorbance of 0.005 or less in cyclohexane, 0.010 to 0.025 in s-tetrachloroethane, depending upon the wave length.

SUMMARY

1-Fluoro-2,4-dinitrobenzene has a potentially extensive usefulness for the determination of primary and secondary amines. The main advantages of the method offered here are that primary and secondary amines can be determined in the presence of tertiary amines, and the method is applicable to amines which are highly soluble in water. Certain amines fail to react with 1-fluoro-2,4-dinitrobenzene because of steric hindrance. The sensitivity of the method permits the determination of quantities in the order of 0.1 micromole of amine.

ACKNOWLEDGMENT

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Determination of Zirconium in Aluminum Alloys

Using p-Bromo- or p-Chloromandelic Acid

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ZIRCONIUM has recently been found useful as a constituent in aluminum-based alloys. The phosphate method for the determination of zirconium (*1*) is lengthy, requires tedious separations, and is subject to error in low zirconium concentration ranges. The alizarin red S colorimetric method is reported to have low tolerance for aluminum ions (*5*, *6*). The success of the mandelate reagents in the determination of zirconium in steels (*3*, *4*) suggests that they might be used to advantage in aluminum alloys. Two procedures for the determination of zirconium in aluminum alloys in the presence of copper, magnesium, silicon, iron, manganese, nickel, tin, antimony, chromium, titanium, and vanadium were developed. The first procedure is applicable to alloys containing less than 0.75% silicon and involves direct precipitation of zirconium with the mandelate reagents. The second procedure is used for alloys containing more than 0.75% silicon and involves a preliminary separation of zirconium as the hydroxide. A procedure for the simultaneous determination of silicon and zirconium in the same sample is also described.

PROCEDURE

Zirconium Determination in Alloys Containing Less Than 0.75% Silicon. Three to five grams of the aluminum sample in a 250-ml. beaker are dissolved in 20 ml. of hydrochloric acid (1 to 1), adding the acid slowly until the vigor of the reaction subsides. Additional acid may be necessary to complete solution if the sample is larger than 3 grams. When dissolution is complete, 25 ml. of water are added, and the solution is boiled for a few minutes. The solution is filtered through a No. 31 Whatman filter paper to remove any undissolved particles or silicigeneous matter. The volume of the solution is adjusted to about 75 ml. while the acid concentration is maintained at around 15% or less. Eighteen milliliters of a 0.1M solution of p-bromo- or p-chloromandelic acid is added with constant stirring. (For amounts of zirconium larger than 0.1% use correspondingly larger amounts of the reagent.) The solution is digested for 20 minutes at 80 to 85° C., cooled, and filtered through a No. 40 Whatman filter paper. The precipitate of zirconium halomandelate is washed about 10 times with distilled water. The paper and precipitate are charred slowly and ignited in a platinum crucible at approximately 1000° C. The final weighing of the zirconium oxide can be performed directly in the platinum crucible or on a tared weighing dish to which the oxide has been transferred.

$$\% \text{ zirconium} = \frac{\text{weight } ZrO_2 \times 0.7403 \times 100}{\text{weight of sample}}$$

With mandelic acid as a reagent the following procedure is used. Three to five grams of the sample are dissolved with 35 ml. of hydrochloric acid (1 to 2), and the contents are filtered through a No. 31 Whatman filter paper. The filtrate is adjusted to about 100 ml., and the zirconium is precipitated with a saturated solution of mandelic acid (amount depending on the zir-

Table I. Determination of Zirconium in Aluminum Alloys Using Various Reagents

Composition of Alloy, %	Zirconium Found, %			
	Phosphate[a]	Mandelic acid	p-Chloro-mandelic acid	p-Bromo-mandelic acid
Al 92.42 (by diff.)	0.06	0.06	0.06	..
Cu 4.64	0.06	0.06	0.06	..
Mg 1.44	0.06	0.06	0.06	..
Mn 0.62	0.06	0.06	0.06	..
Fe 0.38	0.06	0.06	0.06	..
Si 0.31				
Cr 0.09				
Zn 0.04				
Al 92.61 (by diff.)	0.08	0.08	0.08	0.08
Cu 4.55	0.07	0.08	0.08	0.08
Mg 1.32	0.08	0.08	0.08	0.08
Mn 0.53	0.08	0.08	0.08	0.08
Fe 0.47	0.08	0.08	0.08	0.08
Si 0.38				
Cr 0.05				
Zn 0.01				

[a] Method of Aluminum Co. of America (*1*).

Table II. Determination of Added Zirconium in Aluminum Alloys Using Various Reagents

Composition of Alloy, %	Zirconium Added, Gram	Zirconium Found, Gram: Phosphate	Mandelic acid	*p*-Bromomandelic acid
3-S Alloy				
Al 97.71 (by diff.)	0.0040	0.0038	0.0040	0.0040
Mn 1.12	0.0040	0.0039	0.0039	0.0038
Cu 0.12	0.0040	0.0036	0.0038	0.0038
Zn 0.49				
Fe 0.48				
Si 0.05				
Cr 0.03				
17-S Alloy				
Al 93.05 (by diff.)	0.0010	0.0009	0.0010	0.0009
Cu 4.29	0.0010	0.0009	0.0011	0.0009
Mn 0.64	0.0010	0.0008	0.0008	0.0010
Mg 0.64				
Si 0.64	0.0015	0.0014	0.0014	0.0014
Fe 0.63	0.0015	0.0013	0.0014	0.0014
Zn 0.05	0.0015	0.0014	0.0014	0.0014
Cr 0.04				
Ti 0.02	0.0040	0.0036	0.0038	0.0039
	0.0040	0.0038	0.0037	0.0039
	0.0040	0.0038	0.0039	0.0040
18-S Alloy				
Al 91.70 (by diff.)	0.0004	0.0004	0.0003	0.0004
Cu 4.18	0.0004	0.0004	0.0004	0.0004
Ni 2.06				
Fe 0.68	0.0008	0.0007	0.0008	0.0007
Si 0.59	0.0008	0.0007	0.0007	0.0007
Mg 0.58	0.0008	0.0005	0.0007	0.0007
Mn 0.10				
Ti 0.05	0.0015	0.0015	0.0015	0.0015
Zn 0.04	0.0015	0.0012	0.0014	0.0014
Cr 0.02	0.0015	0.0014	0.0015	0.0013
	0.0045	0.0043	0.0044	0.0044
	0.0045	0.0043	0.0043	0.0044
	0.0045	0.0043	0.0044	0.0043
	0.0080	0.0075	0.0078	0.0079
	0.0080	0.0076	0.0078	0.0079
	0.0080	0.0076	0.0078	0.0079
	0.0310	0.0302	0.0304	0.0307
	0.0310	0.0304	0.0304	0.0308

conium content). The zirconium mandelate is filtered on a No. 40 Whatman filter paper with the aid of some paper pulp, the precipitate washed with a warm solution of mandelic acid containing 3% hydrochloric acid, charred slowly in a platinum crucible, ignited, and the zirconium oxide weighed directly in the crucible or transferred to a tared dish and then weighed.

The results obtained by these procedures are given in Tables I and II. In Table I the zirconium was actually present in the alloy. In Table II the zirconium was added as a solution of zirconyl chloride after the sample had been dissolved.

Zirconium Determination in Alloys Containing More Than 0.75% Silicon. Two grams of the aluminum sample in a 250-ml. beaker are dissolved by adding 5 grams of sodium hydroxide pellets followed by 20 ml. of distilled water. The beaker is covered with a watch glass and placed in a cool water bath until the vigor of the reaction has subsided. If necessary, more distilled water (10 to 15 ml.) may be added. Further dissolution is obtained by warming the beaker on a hot plate. A total of 10 ml. of hydrogen peroxide (3%) is then added, small amounts at a time, to effect solution of copper and other undissolved metals. The contents are boiled gently for 10 minutes, cooled, diluted to about 150 ml., and filtered on a No. 31 Whatman filter paper after washing any particles adhering on the watch glass into the beaker.

Zirconium remains in the filter paper as the hydrous oxide. The precipitate is washed well with about 10 small portions of warm distilled water, and the filtrate is discarded. The bulk of the precipitate is washed back into a 250-ml. beaker with about 25 ml. of warm distilled water. Sixty milliliters of warm hydrochloric acid (1 to 3) are then poured on the filter paper, while the funnel is rotated to ensure complete solution of the zirconium. The washings are caught in the beaker containing the bulk of the precipitate. Complete solution of the contents of the beaker is obtained by heating. More acid is added if necessary. The contents are then diluted to about 125 ml., filtered, using a No. 31 Whatman filter paper to remove any residue, and the filtrate is adjusted to an acidity of 12.5 to 20% with hydrochloric acid in a total volume of not more than 200 ml. Twenty-five milliliters of 0.1 *M* *p*-bromo- or *p*-chloromandelic acid is added with constant stirring. (When the approximate content is known, the amount of reagent can be calculated on the basis of theoretical precipitation as the zirconium tetramandelate. Experiment has shown that 16% excess reagent in the case of *p*-bromomandelic acid is required for complete precipitation. When the zirconium content is unknown, an excess amount can be added as above, or an approximate amount added, and the filtrate can be tested with reagent for complete precipitation.) The contents are digested at 80 to 85° C. for 20 minutes, cooled to room temperature, and filtered through a No. 40 Whatman filter paper using some paper pulp as an aid. The precipitate of zirconium halomandelate is washed 10 times with distilled water, and the paper and precipitate are charred slowly and ignited in a preweighed platinum crucible at approximately 1000° C. For ordinary industrial work the zirconium oxide after ignition can be transferred to a tared dish for weighing.

Results obtained on aluminum alloy samples to which a known amount of zirconium was added are given in Table III.

Table III. Determination of Silicon and Added Zirconium in Aluminum Alloys

Composition of Alloy, %	Zirconium Added, Gram	Zirconium Found, Gram: Phosphate	*p*-Chloromandelic acid	*p*-Bromomandelic acid
356-S Alloy				
Al 91.66 (by diff.)	0.0004	0.0003	0.0004	0.0004
Si 7.28	0.0008	0.0007	0.0007	0.0008
Fe 0.48	0.0011	0.0009	0.0010	0.0010
Mg 0.38	0.0011	0.0010	0.0011	0.0011[a]
Cu 0.12	0.0022	0.0020	0.0022	0.0022
Mn 0.05	0.0022	0.0021	0.0021[a]	0.0021[a]
Zn 0.02	0.0044	0.0040	0.0041	0.0043
Ti 0.01	0.0044	....	0.0041[a]	0.0042[a]
	0.0150	0.0142	0.0147	0.0148
	0.0300	0.0291	0.0297	0.0298
	0.0300	....	0.0297[a]	0.0297[a]
355-S Alloy				
Al 92.52 (by diff.)	0.0008	0.0006	.....	0.0008
Si 4.95	0.0011	0.0011	0.0010	0.0010
Cu 1.40	0.0011	0.0010	0.0010[a]	0.0010[a]
Fe 0.48	0.0022	0.0020	0.0021	0.0021
Mg 0.46	0.0028	0.0027	.....	0.0027
Ti 0.11	0.0028	0.0027	.....	0.0027[a]
Mn 0.05	0.0150	0.0142	.....	0.0149
Zn 0.03				
51-S Alloy				
Al 96.74 (by diff.)	0.0015	0.0014	0.0014	0.0014
Si 1.14	0.0015	.....	.....	0.0014[a]
Mg 0.72	0.0028	0.0025	.....	0.0027
Fe 0.64	0.0035	0.0034	0.0033	0.0035
Cr 0.28	0.0042	0.0040	0.0042	0.0040
Cu 0.25	0.0042	0.0040		0.0041[a]
Mn 0.10				
Zn 0.09				
Ti 0.04				

[a] Silicon determined in same sample by method described.

Simultaneous Determination of Silicon (*1*, *2*) and Zirconium in High Silicon Aluminum Alloys. Two grams of the aluminum alloy sample in a large nickel dish are treated with 5 grams of sodium hydroxide pellets, and 20 ml. of distilled water are added, 10 ml. at a time. The dish is covered with a watch glass and cooled by means of a water bath until the vigorous reaction has subsided. When the reaction is near completion, 10 ml. of distilled water is used to wash any undissolved particles adhering to the sides of the dish down into the sirupy mass. The dish is warmed on a hot plate, and 10 ml. of hydrogen peroxide (3%) are added, small amounts at a time, to dissolve copper and other undissolved metals. The contents are moderately boiled for 10 to 15 minutes or until they have the appearance of a semipaste. The mass is diluted to 40 ml., and cooled. It is then transferred into a 600-ml. beaker, containing 50 ml. of a mixture of concentrated sulfuric and phosphoric acids (4 to 1), which has been rotated to moisten the sides with the acids. Fifteen milliliters of a mixture of concentrated hydrochloric and nitric acids in water (1 to 1 to 2 by volume) are then added and the contents taken down to dryness and fumes using medium heat. Fuming is continued for 10 minutes. After cooling, 35 ml. of water and 10 ml. of concentrated hydrochloric acid are added. The silica is removed by filtration through a No. 40 Whatman filter paper using paper pulp as an aid. The silica is washed first with warm distilled water, then with hot saturated ammonium sulfate solution to remove lead sulfate, and again with warm water. The filtrate is dehydrated as described above, the silica removed by filtration, and the combined residues are ignited in a platinum crucible after slow charring to remove carbonaceous material. The crucible and contents are cooled, weighed, and then treated with a few

drops of concentrated sulfuric acid and 10 ml. of hydrofluoric acid (48%). This is heated until dry, ignited, cooled, and weighed. The difference in weight represents silica.

Any residue left in the platinum crucible is fused with potassium acid sulfate, the mass dissolved in hydrochloric or sulfuric acid (1 to 9), and the contents are added to the combined original filtrates which should have a total acidity of 10 to 20% and a total volume of not more than 250 ml. The required amount of halomandelic acid is now added and the zirconium content of the sample determined as described above.

Results obtained by this procedure are given in Table III.

SUMMARY

Zirconium in aluminum alloys can rapidly and conveniently be determined gravimetrically by the mandelate method. The use of *p*-chloro- or *p*-bromomandelic acid is preferred to mandelic acid (*4*). No significant difference exists between the chloro and bromo derivative. These reagents are now available commercially from the H. and S. Chemical Co., 528 Howard St., Buffalo 6, N. Y. and Dajac Laboratories, 511 Lancaster St., Leominster, Mass.

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Separation of Hydrogen Peroxide from Organic Hydroperoxides

Application to Polarographic Analysis of Mixtures

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MIXTURES of hydrogen peroxide and certain organic hydroperoxides have been quantitatively separated. It has been observed in this laboratory that the polarographic wave for hydrogen peroxide can be eliminated entirely, as shown in Figure 1, by complexing the hydrogen peroxide with titanium(IV) ion and precipitating the complex in alkaline solution. The organic hydroperoxides reported here seem to be unaffected by the complexing ion and by its precipitation.

The yellow color formed by reaction of titanium(IV) and hydrogen peroxide is the basis for the colorimetric determination of hydrogen peroxide. According to Schwarz (*2, 3*), the yellow complex formed in sulfuric acid solution has the formula $TiO_2(SO_4)_2^{--}$. The removal of hydrogen peroxide from a mixture of hydrogen peroxide and hydroperoxides by precipitation of the yellow solution with ammonium hydroxide seems to be a new application.

Table I. Recovery of Hydrogen Peroxide

Hydroperoxide Present, Mg.		Hydrogen Peroxide, Mg. Added	Found
3-Pentyl	0.8	50	52
	0.4	38	37
tert-Buty	0.1	25	29
	0.4	38	38
	0.5	38	36
	0.5	101	96
3-Cyclohexeny	0.5	5	4
	0.5	50	53
	0.5	50	54
Cyclohexyl	1.0	50	51
2,5,5-Trimethyl-2-hexyl	0.5	50	52
	1.0	50	47

Polarographic current-voltage curves were measured for solutions containing both hydrogen peroxide and organic hydroperoxide. Titanium ion was added as titanium dioxide dissolved in 1*N* hydrochloric acid, which produced a slightly acid solution. The titanium was precipitated with a slight excess of ammonium hydroxide. The current-voltage curve was then repeated. The decrease in wave height as shown in Figures 1 and 2 is due to the precipitation of hydrogen peroxide. The remaining wave in Figure 2 is due to the organic hydroperoxide.

The applications reported here involve primarily water-soluble organic hydroperoxides. Some mixed solvents have also been tried without adverse effect. Concentrations studied were of the order of $10^{-4}M$ in the solutions measured polarographically.

Mixtures of hydrogen peroxide and the following organic hydroperoxides have been analyzed successfully by this method: 3-pentyl hydroperoxide (1-ethylpropyl hydroperoxide, International Union of Chemistry) *tert*-butyl hydroperoxide, and 3-cyclohexenyl hydroperoxide, cyclohexyl hydroperoxide, and 2,5,5-trimethyl-2-hexyl hydroperoxide (1,1,4,4-tetramethylpentyl hydroperoxide, the International Union of Chemistry). Data showing the results obtained after the addition of known amounts of hydrogen peroxide are shown in Table I. No failures of the method have so far been observed. The method may also be useful with other combinations of hydrogen peroxide, organic hydroperoxides, and peroxides.

EXPERIMENTAL

Polarograms were run with a Sargent Model XX, electronic recording instrument and an H-type polarographic cell (*1*) connected to a saturated calomel electrode with fritted-glass agar bridge. Ten-milliliter portions of solution were used. The drop time was of the order 3 to 4 seconds and the value of *m* was approximately 1.35 mg. per second. The applied voltage was increased at a rate of 1 volt per 5 minutes.

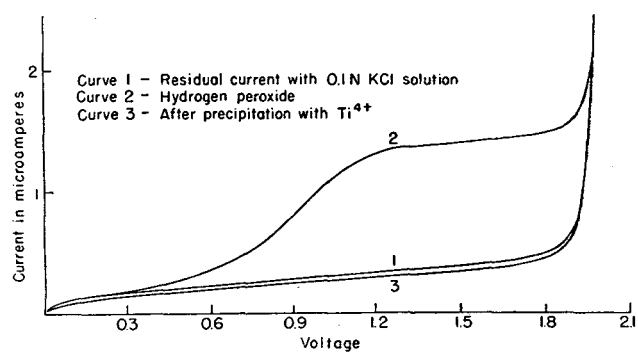


Figure 1. Current-Voltage Curves for Hydrogen Peroxide before and after Treatment with Titanium Ion

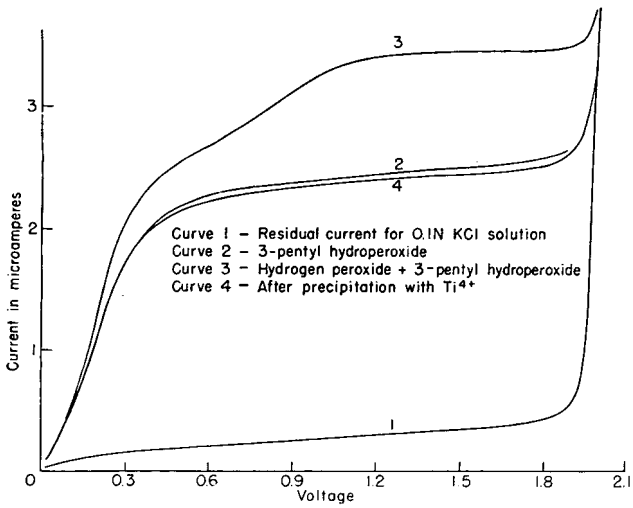


Figure 2. Current-Voltage Curves for Hydrogen Peroxide–3-Pentyl Hydroperoxide

The solutions reported in Figure 1 contained 0.1*N* potassium chloride as supporting electrolyte. Curve 1 represents the residual current. Curve 2 shows the current-voltage curve obtained after 0.02 ml. of a 0.25% hydrogen peroxide solution (approximately 50γ) was added to 10 ml. of 0.1*N* potassium chloride. Curve 3 was obtained after 1 mg. of titanium dioxide in 0.1 ml. of 1*N* hydrochloric acid had been added to the peroxide solution, followed by 1 drop of 6*N* ammonium hydroxide. Curves 1 and 3 are identical except for the slight dilution effect.

Curve 1 of Figure 2 is the residual current for 0.1*N* potassium chloride. Curve 2 was obtained when approximately 0.8 mg. of 3-pentyl hydroperoxide was added to 10 ml. of 0.1*N* potassium chloride. Curve 3 was obtained after the extra addition of 0.02 ml. of 0.25% hydrogen peroxide. Following addition of 1 mg. of titanium dioxide in 0.1 ml. of 1*N* hydrochloric acid and 1 drop of 6*N* ammonium hydroxide, curve 4 was obtained. The slight difference between curves 2 and 4 is approximately equal to the dilution effect.

Upon acidification, the hydrogen peroxide is restored to the solution and a polarographic wave identical with the original wave is obtained. The nature of the precipitate containing the hydrogen peroxide has not yet been determined. The upper limit of concentration at which this separation of hydrogen peroxide and organic hydroperoxide can be achieved also remains to be determined.

This separation is useful analytically, especially when the reduction potentials of hydrogen peroxide and the organic hydroperoxide differ only slightly. The separation will be especially useful, chemically, if it can be carried to higher concentrations.

The extension of this method of separation to mixtures of hydrogen peroxide and other organic hydroperoxides and peroxides is being studied in this laboratory.

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New Flux for Determination of Total Carbon in Silicon Carbide

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METHODS for the determination of total carbon are tedious and subject to possible errors as a result of incomplete combustion of carbon and of manipulative processes required (*1*, *2*). These sources of error have been eliminated or greatly reduced in a new, rapid, accurate, and economical procedure which requires a much lower combustion temperature with the use of a new flux. Results agree with those obtained by the National Bureau of Standards. The combustion is completed in 15 minutes.

REAGENTS AND EQUIPMENT

Red lead tetroxide, Pb_3O_4, C.P.
Cryolite, Na_3AlF_6, powder.
Glass mortar and pestle.
Nickel crucibles, 40-ml. capacity, used as mixing vessels.

PREPARATION OF SAMPLE

The sample of silicon carbide 112 from the National Bureau of Standards was analyzed without any additional preparation. The samples of silicon carbide marked A, B, C, and 240 in Table II were prepared to pass a 120-mesh silk screen.

PROCEDURE FOR SILICON CARBIDE DETERMINATION

The cryolite and red lead, in order to remove any organic matter, are burned off for 15 minutes in the combustion furnace in a stream of oxygen at 820° C. (1500° F.) for the cryolite and 540° C. (1000° F.) for the red lead. After cooling, 20 grams of the cryolite is thoroughly mixed with 100 grams of the red lead, using a glass mortar, and the mixture is placed in a tightly stoppered bottle ready for use. Johnson clay combustion boats are calcined at 1800° F. for 15 minutes in the combustion furnace with a stream of oxygen in order to remove any organic matter. The boats are then placed in a borosilicate glass dish and covered to prevent contamination from dust particles.

A 0.25-gram sample of National Bureau of Standards standard sample silicon carbide 112 is weighed and mixed with 3 grams of the prepared flux in a nickel crucible. Then to this mixture approximately 6 grams of 90-mesh RR Alundum is added and mixed thoroughly. A Johnson clay boat is partly filled with 90-mesh RR Alundum and by means of a $^3/_8$ inch glass rod is grooved or furrowed for the bed. The mixture is then placed in the bedded combustion boat ready for the analysis. After the boat has been inserted in the combustion tube and the predetermined temperature of 1700° to 1750° F. obtained, oxygen is admitted at the rate of 350 ml. per minute for 15 minutes. The carbon dioxide absorption bulb is then disconnected and placed in the balance case for 1 to 2 minutes, during which time the boat can be withdrawn from the furnace. Blanks are run on the mixture as used but without the silicon carbide, so as to determine the true weight of carbon dioxide absorbed.

RESULTS

Table I shows the accuracy that can be obtained by the use of the procedure to determine the total carbon content of National Bureau of Standards standard sample 112 at the temperature of 1700° to 1750° F. for 15 minutes. The average deviation was

Table I. Analysis of National Bureau of Standards Standard Silicon Carbide 112

Temp., °F.	Blanks, Gram CO_2	Total Carbon Found, %	NBS Value, %	Deviation, %
		With Special Flux		
1700–1750	0.0023	29.11	29.12	0.01–0.02
	0.0025	29.10		
	0.0025	29.10		
	0.0024	29.12		
		With Red Lead		
1700–1750	0.0026	28.83	29.12	0.29–0.50
	0.0027	28.80		
	0.0029	28.59		
	0.0028	28.62		

Table II. Reproducibility of Total Carbon Determinations Using Special Flux Mixture

	Standard Value, %	Carbon Found[a], % I	Carbon Found[a], % II
Bureau of Standards silicon carbide 112	29.12	29.11	29.10
		29.11	29.12
		29.10	29.12
		29.11	29.11
		29.10	29.10
		29.10	29.09
		29.09	29.11
Silicon carbide refractory			
A	...	30.45	30.42
B	...	30.26	30.22
C	...	29.48	29.44
Silicon carbide 240	...	29.30	29.31

[a] I and II, duplicate runs at same time in different tubes.

found to be 0.01%. Table I also shows the results obtained by using red lead instead of the special flux at the same temperature and time.

Table II shows the reproducibility of the results obtained with the method. From the successive determinations the average deviation was found to be 0.02%.

A source of error in the determination of carbon is the uncertainty in the weighing of the carbon dioxide absorber unless extraordinary precautions are used. With a bulb that has absorbed 0.3 gram of carbon dioxide, despite blanks of 0.0023 to 0.0025 gram of carbon dioxide, the maximum deviation amounts to 0.03%, and the average deviation is 0.015%. The maximum error is 1 part in 1000. This accuracy in results is due to the consistent time interval for weighing the carbon dioxide absorber throughout the analysis, after the 15-minute combustion time. As variable temperature will affect the weight slightly, it is advisable to weigh at as near a constant temperature as possible. The counterpoise bulb used in weighing should be under the same conditions as the carbon dioxide absorber.

The use of cryolite showed no effect of fluorine on the combustion boats, the combustion tubes, or the glassware in the train. The fluorine that passes off is filtered out by the ironized asbestos and chromic acid solution. Tests were performed to see whether any fluorine was being absorbed by the Ascarite in the carbon dioxide absorption bulb.

Samples were prepared by mixing 0.25 to 0.50 gram of silicon carbide with 3 to 6 grams of the special flux, and blanks were prepared without silicon carbide. The carbon dioxide that was driven off by the burning of these samples was bubbled through a standard solution of titanium (1 mg. of titanium oxide per ml.) which was oxidized with hydrogen peroxide to form the complex. The complex was measured on a photoelectric colorimeter before being inserted at the end of the combustion train. At the end of 15 and 30 minutes the pertitanic acid solution was again measured on the colorimeter; the readings were exactly the same as the original one.

The tests showed that no trace of fluorine vapor was being passed to the carbon dioxide absorber; any fluorine vapor would have bleached the pertitanic acid, which would have shown a discrepancy in the reading on the colorimeter.

The etch test and the lead chlorofluoride test were also performed on the Ascarite used to absorb carbon dioxide, but no trace of fluorine was found.

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Assay of Certain Organic Materials by Dichromate Oxidation

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THE need occasionally arises for a rapid and reasonably accurate determination of organic substances dissolved or suspended in water at concentrations of less than 250 p.p.m. Such was the case when the task was undertaken of measuring the simultaneous adsorptions of starches and of froth flotation collectors on quartz and on hematite. The use of radioactive tracer techniques is impractical with starch, and the dichromate oxidation method described here was found to be more satisfactory for the low concentrations investigated than other ordinarily accepted methods of starch determination. The same general procedure, with suitable variations, was applicable to dilute solutions of starch, laurylamine acetate, or sodium oleate.

The basic reaction involved was the oxidation of organic materials by dichromate to carbon dioxide, water, and certain stable compounds of low molecular weight. Similar procedures have been reported in connection with the oxygen-consuming values of organic wastes (*1, 3–6, 8*). Dichromate has advantages over permanganate as oxidant in several respects, as reported by Medalia (*3*) and Moore *et al.* (*5*). The consumption of dichromate per unit weight of the various starch products, including whole cornstarch, its amylose and amylopectin fractions, and various dextrins and gums derived from starch, was found to be practically independent of the complexity of the carbohydrate molecules, while with permanganate each type of carbohydrate gave slightly different results under otherwise identical conditions (*2, 7*). Furthermore, oxidation by dichromate was amenable to control so that, for instance, starch and laurylamine acetate could be determined separately when present in the same solution.

For quantitative determinations of organic materials in water, an optimum quantity of dichromate reagent was allowed to react with the organic substance at elevated temperature and the excess was then determined either by titration or by a colorimetric procedure. The rate and extent of the oxidation reaction were functions of dichromate and acid concentrations, temperature of reaction, and time. When the acid concentration in the reaction mixture was kept below 4% sulfuric acid (by volume), satisfactory results could be obtained in the oxidation of starches, but lauryl amine acetate was attacked only slightly. Laurylamine acetate was sufficiently oxidized at acid concentrations above 35% for satisfactory quantitative determinations. Typical oxidation results at various acid strengths are shown in Figure 1. The curve for oxidation of dextrose also applies to all other starch products

studied. The percentage reactions were calculated from the idealized reactions:

$$(C_6H_{10}O_5)_x + 12x\,(O) = 6x\,CO_2 + 5x\,H_2O \quad (1)$$

$$CH_3(CH_2)_{11}NH_3(CH_3COO) + 36(O) = 12CO_2 + 12H_2O + NH_4(CH_3COO) \quad (2)$$

$$K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3(O) \quad (3)$$

Variations in rate and extent of reaction with dichromate concentration were such that the dichromate consumed in various reaction mixtures was proportional to the amount of organic material initially present, provided the conditions of time and temperature allowed at least 10% reaction, and that the final dichromate concentration in the reaction mixture was at least 0.002*M*.

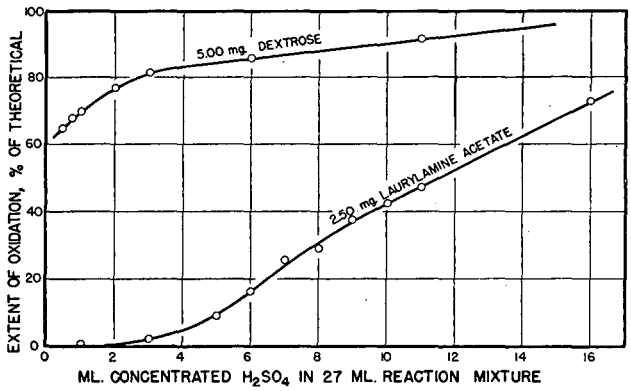


Figure 1. Effect of Acidity of Reaction Mixture on Extent of Oxidation with Dichromate

In no cases were the oxidation reactions stoichiometrically complete, although the more acid, the higher the temperature of reaction, or the longer the time allowed, the greater was the extent of reaction. The analytical results were based on known solutions run simultaneously with the unknowns. The oxidation reaction did not proceed measurably at room temperature under the conditions employed here. Although satisfactory results were obtained by heating the reaction mixtures in a boiling water bath for about 2 hours, it was more convenient to heat them for 0.5 hour at 120° C. in an autoclave to attain the same extent of reaction. One of the most important details of the whole analytical procedure is that the reaction time and temperature must be identical for all mixtures of a series, which includes necessary reference solutions containing known amounts of the material being determined.

REAGENTS AND PROCEDURE

Permanganate, approximately 0.1*N* potassium permanganate.

Ferrous ammonium sulfate; 40 grams of ferrous ammonium sulfate and 10 ml. of sulfuric acid per liter.

Dichromate, 25 grams of potassium dichromate per liter of 1 to 1 sulfuric acid.

Sulfuric acid, analytical grade.

Phosphoric acid, USP grade.

Only relative reagent concentrations were ordinarily required, as the analytical results were based on the simultaneous determinations of known solutions of the material being analyzed.

ANALYTICAL PROCEDURES

Determinations of Starches. Prepare reaction mixtures of known and unknown solutions in 250-ml. Erlenmeyer flasks by adding 2.00 ml. of dichromate reagent to 25 ml. or less of the starch solution containing not more than 5.0 mg. of starch, in each case bringing the final volume to 27.0 ml. Heat all preparations simultaneously in an autoclave at 120° C. for 0.5 hour, or at 100° C. for 2 hours. Cool, add 2 ml. of concentrated phosphoric acid, titrate with 0.05*N* ferrous ammonium sulfate, and add an excess of 4 ml. Back-titrate the excess ferrous ion with 0.1*N* potassium permanganate. Calculate amount of starch present on the basis of titrations of the known solutions.

Table I. Relative Extent of Oxidation of Several Starch Products Assayed by Dichromate Oxidation

Starch Product	Reduction Value
Dextrose	1.000 (basis)
Gum 3502 (British gum type of modified cornstarch)	0.999
B-fraction of cornstarch (amylose)	0.990
Pearl starch (unaltered whole cornstarch)	0.96
Dextrin 156 (pyrodextrin type of modified cornstarch)	1.003
Dextrin D	0.995
Oxidized starch (18.9% carboxyl)	0.793

In the case of the partially soluble starches, centrifugally cleared solutions were used in the adsorption tests, and the analyses were based on standard solutions of dextrose. Table I gives the relative extent of oxidation of various starch products when treated in the foregoing manner. The ideal value for all but the "oxidized starch" is 1.000; that for the oxidized starch is 0.815 because it contains 18.9% carboxyl groups by weight. The variations of actual values from the ideal may be attributed to experimental errors and slight variations in moisture content of the air-dried starches employed.

Determination of Laurylamine Acetate. Prepare reaction mixtures of known and unknown amine solutions in 250-ml. Erlenmeyer flasks by adding 3.00 ml. of dichromate reagent to 10 ml. or less of the amine solution containing not more than 2.5 mg. of laurylamine acetate. Add 10.0 ml. of concentrated sulfuric acid from a buret while swirling to prevent spattering, and bring the total volume to 23.0 ml. Heat all preparations simultaneously in an autoclave at 120° C. for 1 hour. Cool, dilute with 50 ml. of water, add 3 ml. of concentrated phosphoric acid and titrate as for the starch determinations.

Determinations of Starch and Laurylamine Acetate in Solutions Containing Both. Prepare and run two sets of reaction mixtures, one as for starch and the other as for laurylamine acetate determinations, except that for the amine sample, one half the weight of the starch plus the weight of amine present must not exceed 2.5 mg.

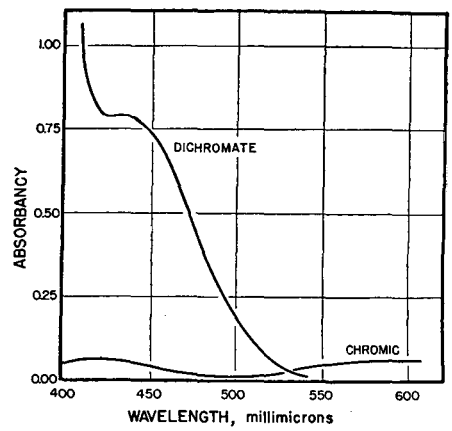


Figure 2. Spectral Absorption Curves for Dichromate and Chromic Ions

Chromium, 150 mg. per liter, in 0.4*N* sulfuric acid

Alternative Colorimetric Procedure. The excess dichromate in the reaction mixtures following the oxidation reactions may be determined colorimetrically if the solutions are clear and free of interfering colored substances. In this case, the solutions as they are removed from the autoclave are diluted accurately to 100 ml. and their color densities then measured in a Beckman spectrophotometer at an arbitrary wave length in the visible range of

422 to 440 mμ. The absorbancies of dichromate solutions are relatively insensitive to slight variations in wave length over this range, as can be seen from the spectral absorption curves shown in Figure 2. Experimental evidence showed that both dichromate and trivalent chromic ion concentrations under these conditions were directly proportional to the measured absorbancies of their solutions.

Discussion. The analytical procedures in the absence of chloride ion as outlined were as precise as the various reagent measurements. The dichromate reagent was measured from a 5-ml. microburet; the reagent was allowed to flow from the buret at the same rate and over the same range of the volumetric scale for each sample, to eliminate drainage errors. The exact quantity of reagent added was not defined, but each sample received exactly the same quantity. The permanganate titration was also performed with a 5-ml. microburet and corrected for indicator blank. The precision of measurement attained for the over-all procedure was about ±0.02 ml. of the 0.1*N* potassium permanganate, ±0.02 mg. of starch, or ±0.01 mg. of laurylamine acetate in the samples of their pure solutions taken for analysis. Sodium oleate responded similarly to the laurylamine acetate in wet combustion tests.

Only small amounts of chloride could be tolerated in the high-acid reaction mixtures, and then suitable blanks were necessary. Samples containing more than 0.02 meq. of chloride ion were unsuitable because of the uncertain amount of dichromate consumption through oxidation of the chloride in the strongly acid reaction mixtures.

As satisfactory results were obtained without employing catalysts in the oxidation step (*5*, *6*), the effect of silver and other metallic ions on the oxidation reaction was not investigated.

ACKNOWLEDGMENT

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Determination of Primary Fatty Amines in Amine Mixtures

Potentiometric Titration Techniques

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TITRATION in nonaqueous media with perchloric acid has been found to be more satisfactory than the Van Slyke procedure for the determination of the amino acids (*1*). This procedure has been adapted to the determination of the amine number of mixtures of fatty amine products of high molecular weight (*2*). The perchloric acid titration, however, does not differentiate between the primary amines and the secondary and tertiary amines in a mixture.

To effect such a differentiation between primary amines and secondary and tertiary amines, Wagner, Brown, and Peters (*3*) potentiometrically titrated methanol solutions of aromatic and short-chain aliphatic amine mixtures after treatment with salicylaldehyde to neutralize the primary amines as azomethines. Under these conditions the secondary (plus tertiary) amine content of the amine mixtures is equivalent to the acid used in titrating to the first end point. Primary amine is then calculated by difference from a separate determination of total base.

This procedure is not directly applicable to the fatty amines of high molecular weight because of their poor solubility in methanol (and isopropyl alcohol). However, these products are soluble in chloroform, even after the addition of some water in isopropyl alcohol. By this modification the method can be used to determine the primary amine content of a mixture of long-chain fatty amines.

The experimental results shown in Tables I and II illustrate the scope and accuracy of the Wagner, Brown, and Peters method when adapted to the analysis of fatty amines of high molecular weight as described here. This method is particularly effective for the analysis of long-chain fatty amine derivatives which contain both a primary and a secondary amino group in the same molecule. Such compounds are not completely soluble in the Van Slyke reaction mixture, and by the Van Slyke procedure appear to contain almost 200% of primary amino nitrogen. Using the procedure described here, such compounds have been titrated quantitatively both for total amino group content and for secondary amino group content. Results from the titration of such a compound, α-octadecylaminopropylamine, are included in Table I.

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EQUIPMENT

The instrument used for the potentiometric titrations in this study was a Central Scientific Co. titration-pH meter. However, any pH meter which can be adapted to titrations may be used. The procedure should be readily adaptable to industrial recording titrators.

The electrodes were the ordinary, full-range, industrial glass and calomel electrodes obtainable from the Beckman Instrument Co.

A 10-ml. microburet is recommended for these titrations.

REAGENTS

Chloroform, analytical reagent grade.

Salicylaldehyde, free of salicylic acid.

A 5% solution of distilled water in isopropyl alcohol.

Hydrochloric acid, 0.5*N* in isopropyl alcohol, prepared by adding one volume of concentrated C.P. hydrochloric acid to isopropyl alcohol, diluting with the alcohol to 24 volumes, and standardizing against anhydrous sodium carbonate by potentiometric titration in aqueous solution. This reagent has been used for as long as 30 days in cool weather without noticeable deterioration. In warm weather precautions should be taken to avoid errors caused by the high coefficient of thermal expansion and volatility.

PROCEDURES

Determination of Total Base. To a 1-gram sample of the high molecular weight fatty amine mixture in 90 ml. of chloroform, add 10 ml. of the 5% solution of water in isopropyl alcohol, and titrate potentiometrically with 0.5*N* hydrochloric acid in isopropyl alcohol. (To simplify the comparison of the titrations with and without added salicylaldehyde, 5 or 6 grams of sample may

Table I. Experimental Results from Potentiometric Titration of Amine Mixtures of Known Composition

Description of Sample	% Composition Calcd. from Potentiometric Titration Results: Primary amine	Secondary amine	Theoretical Primary Amine Content, %
Known mixture[a]	28.2	...	28.2
Known mixture[a]	42.7	...	42.8
Known mixture[a]	56.4	...	56.1
Known mixture[a]	97.4	...	97.6
Known mixture[a]	17.7	...	17.7
Dioctadecylamine	0.0	100.2	0.0
γ-Octadecylaminopropylamine	97.8	98.2	99.0[b]
N-Dodecylethylenediamine	97.3	97.8	98.6[c]
3-Isopropylaminopropylamine	98.9	98.3	99.0[b]

[a] Contained weighed amounts of octadecylamine, dioctadecylamine, and *N*-methyldioctadecylamine.
[b] Values represent presumed purity of samples based on source and purification procedures.
[c] Based on theoretical total amine number as determined by perchloric acid titration.

Table II. Experimental Results from Potentiometric Titration of Some Crude Amine Mixtures

% Composition Calcd. from Potentiometric Titration Results[a]: Primary amine	Secondary amine	Calcd. Amine No.[b]	Amine No. by $HClO_4$ Method (*E*)
87.7	9.64	193.4	193.6
97.6	2.40	205.9	206.1
95.4	0.65	199.6	199.7
76.2	20.42	180.7	180.1
78.3	19.31	183.8	184.0
77.4	11.10	173.3	172.7
93.9	2.29	206.6	208.0
95.5	2.50	206.8	206.9

[a] Based on assumption that secondary amine was only basic contaminant of primary amine present. Method of preparation of these samples made this a reasonably valid assumption.
[b] Calculated from composition of mixture as determined by potentiometric titration. Theoretical amine number of octadecylamine, 208.55. Theoretical amine number of dioctadecylamine, 107.68.

be weighed into a 100-ml. volumetric flask, and dissolved in chloroform, and aliquots of this solution diluted to the concentrations described above. This procedure may not be feasible for some amine mixtures containing large amounts of secondary amine, as secondary long-chain fatty amines are rather poorly soluble even in chloroform. For such samples, it will be necessary to weigh the amine mixture directly into a titration beaker and dissolve as described above.)

pH readings will drop 4 to 5 units at the end point. The exact end point is the mid-point of this rapidly dropping portion of the curve. The end point thus determined represents the amount of 0.5*N* hydrochloric acid required to neutralize all of the amine in the mixture.

Determination of Secondary-Tertiary Amine. To a 5-gram sample of the amine mixture in 90 ml. of chloroform, add 5 to 6 ml. of salicylaldehyde and allow to stand 30 min. at room temperature. (Samples containing large amounts of primary amine may develop a precipitate after a few minutes, but this precipitate will not affect the end point.) After 30 minutes have elapsed, add 10 ml. of the solution of 5% water in isopropyl alcohol and titrate. Add the acid in small increments (0.1 to 0.2 ml.), as this titration may be very small. At the end point, the pH will drop abruptly 1 to 3 units. Plot the titration curve and determine the mid-point of the rapidly dropping portion of the curve. The end point thus determined represents the amount of acid required to neutralize the secondary (plus tertiary) amine in the mixture. (Figure 1 shows a typical pair of titration curves.)

Determination of Primary Amine. The difference between these two titrations, equated to a common sample weight, represents the 0.5*N* hydrochloric acid equivalent to the primary amine in the mixture.

REMARKS

Because carbonates of the fatty amines are insoluble in the solvent used here, the amine samples should be protected as much as possible from carbon dioxide in the air. If carbonates are present, they may be decomposed by heating the sample at 100° C. in vacuo. Samples should be weighed rapidly and if solid, in as large pieces as possible. When fresh samples are not available, the exposed surfaces of the old samples should be removed and discarded before a portion is taken for analysis. Dissolved ammonia, remaining from the nitrile reduction procedure, may be present in crude samples of these high molecular weight fatty amines. To drive off any dissolved ammonia, the chloroform solution of crude amine mixtures should be boiled gently 1 or 2 minutes on a steam bath. When samples have been weighed into beakers and dissolved in chloroform, as described above, the chloroform lost by evaporation during this boiling should be replaced by adding 5 or 10 ml. of additional chloroform after the solutions have cooled to room temperature.

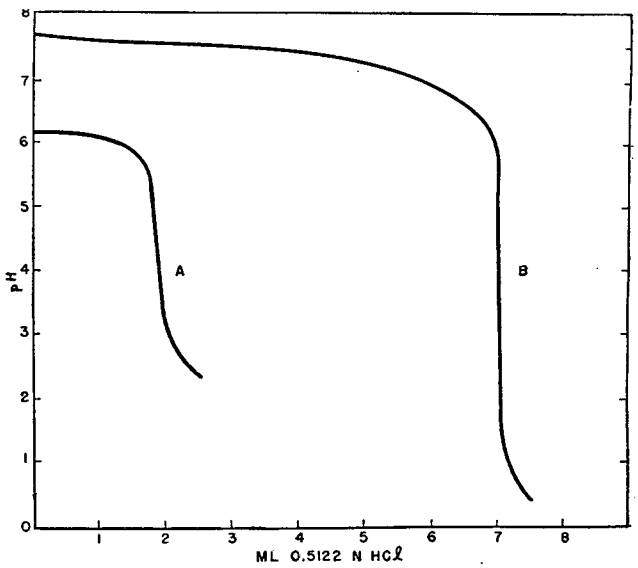


Figure 1. Typical Titration Curves

A. Titration of 50-ml. aliquot after treatment with salicylaldehyde
B. 20-ml. aliquot titrated without salicylaldehyde pretreatment
Sample size 5.6529 grams of crude amine mixture in 100 ml. of chloroform
Data show 76.4% octadecylamine and 18.1% dioctadecylamine

When the alternative, aliquot procedure is used, add 40 or 50 ml. of chloroform to the sample weighed into a 100-ml. volumetric flask, and boil the solution 1 or 2 minutes after the sample has dissolved. Remove the flask from the steam bath, and after a moment of cooling (to avoid boiling over) add chloroform nearly to the mark on the volumetric. Complete the dilution after the solution has cooled to room temperature.

The water–isopropyl alcohol solution is added to the chloroform solution of the amine sample to improve the shape of the titration curve and to improve the accuracy of very small secondary amine titrations. To avoid throwing the amines out of solution, the water–isopropyl alcohol solution must be added only after adequate dilution of the chloroform solution. When chloroform alone is used as a solvent, the pH meter reacts as if one of the electrodes were disconnected, until 1 or 2 ml. of the aqueous isopropyl alcohol titrant have been added. The titration curve then rises to a maximum, levels briefly, and shows the characteristic end-point drop and inflection as the titration is continued. Although this behavior does not affect the accuracy of large titrations, very small titrations are of doubtful value. When the water–isopropyl alcohol solution has been added to the chloroform solution of the amine, more normal titration curves are obtained (Figure 1).

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Field Method for Determination of Traces of Arsenic in Soils

Confined Spot Procedure Using a Modified Gutzeit Apparatus

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In a continuation of the geochemical prospecting research program of the U. S. Geological Survey (*4*), a field method for the rapid estimation of traces of arsenic in soils has been developed. Small anomalies of cobalt in soil have been shown to indicate hidden cobalt ore deposits in the Blackbird area, Idaho (*3*), where some of the ore consists of cobalt minerals containing arsenic. Some evidence indicates that under the weathering conditions at this locality arsenic is more tenaciously retained in soils overlying cobalt ore than is cobalt; for this reason, tests for arsenic may indicate cobalt ore bodies hidden beneath soils, and analyses for both cobalt and arsenic may provide stronger evidence for ore bodies than analyses for cobalt alone. Similar geochemical patterns may exist where ore other than cobalt is associated with arsenic.

Traces of arsenic are generally determined by either the Gutzeit method or the molybdenum blue method. Although reduction to the molybdenum blue complex is a very sensitive test, it is not suitable under field conditions because silica and phosphate interfere and a preliminary distillation is required (*8*).

As none of the macro constituents present in ordinary soils interfere with the Gutzeit method for the determination of arsenic, this method is satisfactory in modified form for field use. The sample is dissolved by fusing a wetted sample with potassium hydroxide. The alkaline fusion of the sample attacks the silicates and arsenic compounds in the sample without loss of volatile arsenic compounds. Zinc is then added to an acidified aliquot in the Gutzeit apparatus, and the gases are passed through lead acetate to a confined spot on mercuric chloride paper. The principle of the confined spot as applied to arsenic analysis has been described by Lachele (*6*). In the present modified method arsine is passed through a section of glass pipe (Figure 1) to the mercuric chloride paper.

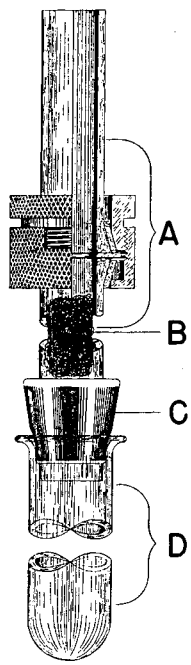


Figure 1. Gutzeit Apparatus Modified for Use in the Field

The reaction of mercuric chloride with hydrogen sulfide is prevented by filling the glass pipe with glass wool previously saturated with lead acetate (*2*). The lead acetate reacts with the hydrogen sulfide before it can reach the mercuric chloride. As lead sulfide is black, it is obvious when the lead acetate is used up. If an adequate amount of lead acetate is used, traces of arsenic can be determined in the presence of large amounts of sulfides. Moderate amounts of antimony do not interfere.

Preparation of standard arsenic spots has been a troublesome factor in using the Gutzeit method of analysis. The arsenic spots fade on standing, and the shade varies with moisture content. Henly (*5*) was the first to use water colors to match arsenic spots prepared from standard solutions, and this principle is used here to prepare permanent standard artificial spots.

At least eight samples can be analyzed for arsenic in 90 minutes. This speed is attained by fusing the soil with potassium hydroxide rather than attacking it with oxidizing acids or the usual flux of sodium carbonate with added potassium nitrate. The potassium hydroxide is considered adequate for sample decomposition, because even the minute amounts of arsenic present in nonmineralized soils can be isolated by this decomposition procedure.

A suitable sensitivity is also obtained by the present modified Gutzeit procedure, as amounts of arsenic as low as 5 p.p.m. can be determined in a 0.1-gram soil sample. This quantity is listed by Rankama and Sahama (*7*) as the average content of arsenic in igneous rock.

Several variable factors affect the accuracy of a determination by the Gutzeit procedure, such as the rate of evolution of hydrogen, the amount of arsenic remaining behind and not swept out, and adsorption of arsine on the lead acetate (*1*). In spite of these variables, the Gutzeit procedure when modified as a field test gave satisfactory results. The arsenic content of a nonmineralized soil sample determined by the field test differs insignificantly to the prospector from the amount determined by a careful laboratory analysis. The difference is even less for mineralized soil samples. The important range from 50 to 2000 p.p.m. is covered by using the 2-ml. aliquot described in the procedure. Concentrations of arsenic above and below this range are determined by inversely varying the size of the aliquot. The data in Table II on soils collected in mineralized areas indicate that the method is suitable for use in geochemical prospecting.

STANDARD ARTIFICIAL SPOTS

Prepare standard artificial spots from chrome yellow and deep chrome yellow water colors for 1, 2, 4, 10, 20, and 40γ of arsenic. Disperse deep chrome yellow water color with 2 ml. of water in a small beaker, paint on filter paper, and allow to dry. Prepare several shades by varying the number of coats of water color per spot, then add 0.5 ml. of water to the beaker and again paint several shades on filter paper. Prepare shades of chrome yellow in a similar manner. Allow to dry. Prepare four spots from solutions containing 1γ of arsenic in the manner described below. Compare these spots with the dry paper that has been colored with water colors, and select and punch out a spot of water-colored paper that matches as nearly as possible the average of the 1γ arsenic spots. Similarly, prepare artificial spots representing 2, 4, 10, 20, and 40γ of arsenic. The series of spots represents 50, 100, 200, 500, 1000, and 2000 p.p.m. when the usual 0.1-gram sample is used.

GUTZEIT APPARATUS

A. Two sections of glass pipe with aluminum coupling, inner diameter 0.25 inch and length 6 inches, obtainable from Fischer & Porter Co., Hatboro, Pa.
B. Lead acetate on glass wool.
C. No. 4 one-hole rubber stopper.
D. Test tube with rim, borosilicate glass, 25 × 150 mm.
Resin demineralizer. Pass tap water through a resin demineralizer to free of arsenic.

PROCEDURE

Prepare the reactive filter of mercuric chloride paper by placing a 0.5-inch square of the paper on the washer between the glass pipes. Fasten in place by screwing the aluminum coupling together.

Transfer to a nickel crucible a 0.1-gram soil sample that has been ground to pass through an 80-mesh sieve. Add 4 pellets (about 0.5 gram) of potassium hydroxide and about 5 drops of water to wet the soil. Heat over a gasoline stove until the water evaporates, and then fuse for about 2 minutes. Allow the crucible to cool, add 3 ml. of water, and stir with a stirring rod until the melt dissolves. Transfer to a 10-ml. graduated cylinder. Add 3 ml. of concentrated hydrochloric acid to the nickel crucible, stir, and combine with the original extract. Dilute to 10 ml. with water, then mix the solution. Transfer a 2-ml. aliquot to a test tube, add 2 ml. of concentrated hydrochloric acid, then

Table I. Determination of Known Amounts of Arsenic Added to Soil[a]

Arsenic Added, γ	Arsenic Found, γ	Average, γ	Average, P.P.M.
1.0	1.0, 1.0, 1.0, 1.0, 1.5	1.1	11
2.5	3, 3, 3, 2, 3	2.8	28
5.0	5, 4, 5, 4, 5	4.6	46
12.0	12, 12, 12, 13, 12	12.1	121
20.0	19, 20, 18, 17, 16	18	180
40.0	40, 40, 30, 40, 25	35	350

[a] Analyses by K. T. Williams and R. R. Whetstone, U. S. Department of Agriculture. The 0.1-gram samples used contained 0.03γ of arsenic; this amount would have a negligible effect on the determination of added arsenic.

add 0.5 ml. of 10% stannous chloride solution, and dilute to 10 ml. with water. Add a 2- to 4-gram piece of mossy zinc, and quickly insert the rubber stopper holding the glass pipe of the Gutzeit apparatus. Let stand 1 hour. Remove the mercuric chloride paper and compare with standard artificial spots. Determine the arsenic content of samples containing more than 2000 p.p.m. by transferring a smaller aliquot to the test tube, adding 2 ml. of concentrated hydrochloric acid, and continuing as directed in the procedure.

RESULTS

In the ranges of arsenic concentrations of importance for prospecting, the precision and dependability of the field method are shown in Table I. Known quantities of arsenic were added to samples of soils of negligible arsenic content, and arsenic was determined by the field method. These experiments show that the simple field method gives reproducible values close to the true arsenic content and should be useful in outlining anomalies in arsenic content.

A series of soil samples was collected at increasing depths from the Blackbird area, Idaho, and analyzed for cobalt and arsenic. Both cobalt content and arsenic content increased with increasing depth. As shown in Table II, the increase in cobalt content from the surface to a depth of 12 feet at location A is 700 p.p.m., whereas the increase in arsenic is 7600 p.p.m. These data indicate that determination of arsenic in soils may be important in finding ore in certain localities.

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Table II. Increase in Cobalt and Arsenic with Depth in Soils Overlying Cobalt Ore

Location	Depth of Sample, Feet	Cobalt, P.P.M.	Arsenic, P.P.M.
A	0	100	400
	2	400	2000
	4	300	4000
	12	800	8000
B	0	70	300
	2	200	700
C	0	55	100
	2	100	600

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Rapid Accurate Determination of Carbohydrates and Other Substances with the Dichromate Heat-of-Dilution Method

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A SIMPLE dichromate oxidation technique was recently developed for the determination of moisture in fruits and vegetables (*5, 8*). The oxidation values for such foods were found to be very reproducible (standard deviations, 0.1 to 0.3%), and the oxidation values for standard samples (National Bureau of Standards) of glucose and sucrose were close to theory. The technique dispenses with the usual external heating by utilizing the heat of dilution of concentrated sulfuric acid, and is thus very rapid, requiring a total time of about 5 minutes per weighed specimen. Thus, the technique should find application in the rapid and accurate determination of certain types of pure organic substances in the presence of water and other nonoxidizables, or in the analysis of binary mixtures of pure substances, or as a simple aid in the determination of chemical composition.

This report deals with an investigation of the scope and limitations of the technique, as applied to starch, typical sugars, and various other types of organic substances. Application to various types of celluloses, involving special problems, has been described (*4*).

METHOD

All operations were performed in watch-glass–covered beakers by using the following procedure.

The test specimen, calculated to reduce 80%, approximate upper limit, of the dichromate—for example, 0.15 gram of benzoic acid or 2.5 grams of sodium oxalate—was weighed out and 25.00 ml. of 1.835*N* potassium dichromate was added. (This solution contained 90.00 grams per liter of reagent-grade potassium dichromate crystals, dried overnight at 100° to 140° C. The solution was filtered before use, and no other precautions were found necessary in order to secure within 0.05% of nominal concentration when the solution was standardized against National Bureau of Standards oxidimetric standard potassium dichromate.) Then 10 ml. of concentrated sulfuric acid, reagent grade, d. 1.84, was slowly added (10 to 15 seconds) to the well-stirred solution or mixture. Efficient stirring without splashing, easily accomplished by means of a magnetic stirrer, was required to avoid reduction of the sulfuric acid. After foaming had moderated, which usually required 15 seconds, 30 ml. more of the acid was rapidly added. After 10 minutes, 150 ml. of water was added and the excess dichromate was titrated whenever convenient. Actually, a 3-minute standing time before titration was found to give maximum yield for typical carbohydrates, aliphatics, and most aromatics, with the exceptions of anthranilic acid and nitrophenol, which gave 0.5% lower yield at the 3-minute point. However, 10 minutes permitted the most efficient utilization of time in the analysis of series of replicates. Blank determinations gave no reduction in titer.

The excess dichromate was determined by electrometric titration of the entire solution without further dilution, using 0.5*M* ferrous ammonium sulfate (0.2*M* in sulfuric acid). This solution is not stable and should be standardized against the dichromate

Table I. Results on Starch, Sugars, Aliphatics, and Aromatics

Substance	Yield, % of Theoretical	Standard Deviations	No. of Replicates
Starch	99.35	0.21	10
Glucose	99.40	0.12	12
Fructose	99.40	0.17	10
Sucrose	99.25	0.09	10
l-Arabinose	99.60	0.12	6
l-Arabitol	99.35	0.18	10
α-Methyl mannoside	99.25	0.10	8
Galacturonic acid.H_2O	99.60	0.15	10
Methyl galacturonide.$2H_2O$	99.40	0.14	6
Methyl galacturonide Me ester.H_2O	99.45	0.17	10
Trimethyl methyl mannoside	99.65	0.06	5
Formic acid	99.95	0.15	8
Oxalic acid (Na salt)	100.00	0.04	9
Glycolic acid	99.85	0.10	7
Methanol	99.50	0.34	5
Glycerol	100.00	0.13	6
Malonic acid	99.85	0.08	6
Tartaric acid (Na salt.$2H_2O$)	99.60	0.07	10
Maleic acid	99.85	0.07	9
Citric acid (Na salt.$2H_2O$)	99.35	0.13	10
Inositol	99.30	0.15	10
Benzoic acid	99.30	0.34	10
Phthalic acid (KH salt)	99.25	0.16	6
Anisic acid	98.60	0.40	6
Anthranilic acid	99.05	0.18	6
p-Nitrophenol	98.65	0.35	6

solution before and after a series of titrations. A simple procedure was to add 5.00 ml. of the dichromate solution to a solution which had just been titrated, and then to retitrate to the same end point. Commercial titrating equipment may be used; the writers prefer a simple arrangement consisting of an inexpensive microammeter (1 μa. per division), a radio potentiometer (500 to 5000 ohms), a 6-volt dry battery, and a tungsten, Nichrome, or calomel electrode versus a positive platinum electrode. Additional details and a discussion of other dichromate methods have been reported (*5*).

MATERIALS

The sucrose, sodium oxalate, and benzoic and anisic acids were standard samples from the National Bureau of Standards and were used without corrections for moisture and ash. The fructose was a purified commercial product.

The starch was a highly purified material prepared from potatoes by A. L. Potter of this laboratory, and was found to have 0.004% amino nitrogen. Ash was 0.25%. Moisture was determined with a vacuum oven at 3 mm. of mercury and 100° C. for 5 hours.

The rest of the sugars were prepared and purified by R. M. McCready of this laboratory. The other substances were the best obtainable commercially and were used without further purification. Ash and moisture values were in general very low. Ash was determined, after precharring, at 550° C., usually for 16 hours. Moisture was determined for the other substances with the Karl Fischer reagent, with the following exceptions: Fructose, nonhygroscopic in any case, was stored for 6 days in vacuo over anhydrous magnesium perchlorate and used without moisture correction. The moisture in arabinose and arabitol was measured with a vacuum oven at 3 mm. of mercury and 60° C. for 16 hours, that in sodium citrate with a circulating-air oven at 105° C. for 1 hour, and that in formic acid, by titration. Carbon and hydrogen combustion analyses were made on trimethyl methyl mannoside. A small amount of sodium hydroxide solution was added to the benzoic, anisic, and anthranilic acids before addition of dichromate, as they are not sufficiently soluble in, or easily wetted by, the reagent.

RESULTS AND DISCUSSION

The results obtained by applying the method to various types of substances are shown in Tables I and II. The yield values were based upon the assumption that dichromate is reduced to the chromic state (Cr^{+++}), that all carbon is oxidized to carbon dioxide, and that no other valence changes occurred (with the one exception of nitrophenol, whose nitrogen is oxidized from +3 to +5).

The following is a typical calculation of yield: 1.0000 gram of *l*-arabinose, containing 0.10% ash and 0.15% moisture, reduced 72.11 ml. of 1.835*N* dichromate. This becomes 72.29 ml. on the dry, ashless basis, and gives 72.29 × 0.001 × 1.835 × 150.13 (formula weight of arabinose) = 19.915 equivalents per mole. Since complete oxidation to carbon dioxide corresponds to 20 equivalents per mole, the yield is 19.915/20 = 0.9960, which is expressed in per cent in Table I. The yields are mean values of the indicated numbers of replicates and the standard deviations refer to deviations of individual values from the means. The yields are expressed to the nearest 0.05%, as that was the approximate combined titrational uncertainty in a mean of six replicates, exclusive of uncertainties in the moisture and ash determinations. These yields may be compared with others for a variety of substances using external heating methods (*1–3, 6, 7*).

Table II. Examples of Incomplete Oxidation

Substance	Yield, % of Theoretical	Standard Deviations	No. of Replicates
With CH_3—or CH_2 groups			
Ethyl alcohol	35	1.2	6
Acetic acid (Na salt)	3	9	6
Propionic acid	62	1.2	6
Succinic acid (Na salt.$6H_2O$)	60	5	9
Malic acid	94	0.8	10
Lactic acid (Ca salt)	38	0.9	6
Lauric acid	72	2	10
Stearic acid (Na salt)	46	8	5
l-Rhamnose.H_2O	70.6	0.15	6
With nitrogen			
Glycine	27	2	3
Serine	96.7	0.13	6
Brucine	96.5	0.6	6
Nicotinic acid	0.8	11	3
Nitromethane	6	10	3
Acetamide	2		6

The yields in Table I are all above 99% except for certain aromatics, in which a time effect was noted, indicating that oxidation may not be complete in these particular cases. On the other hand, results slightly under 100% are to be expected, considering the probable systematic errors. In the moisture and ash determinations traces of moisture (*7*) and nonoxidizable volatile material may have escaped detection. Volatile substances may be partially lost before oxidation can occur. Methanol, for example, gave variable results, 3 to 7% low, when oxidized as usual in a beaker, but gave essentially quantitative results when a reflux condenser (the only instance in Table I) was used.

Finally, results lower than theoretical may be caused by carbon monoxide formation, as noted by others. Christensen and coworkers (*2, 3*), using drastic conditions under which not only carbon monoxide but also oxygen is evolved, found it necessary to oxidize the carbon monoxide with a platinum heater to obtain quantitative results. Segal, Tripp, Tripp, and Conrad (*7*) found that approximately 1.0% of glucose and sucrose was converted to carbon monoxide under the conditions of their experiments, considerably more than under present conditions, although their results with sodium oxalate were almost identical with that in Table I.

The method was tested with known binary mixtures of pure substances (*1*). As models, mixtures of glucose and sucrose were blended in a series of proportions ranging from 5 to 95%. Upon analysis, the mean departure from the known values, or mean error, was 1.2%. The error is of course higher the smaller the difference between the equivalent weights of the two components, which for glucose and sucrose is only 5%. Two other series of binary mixtures, benzoic-phthalic acids and formic-oxalic acids, gave mean errors of 0.4 and 0.1%, respectively.

The types of substances listed in Table II resist oxidation by dichromate to various extents in the present method, and yields were not improved by use of prewarmed (60° C.) concentrated sulfuric acid. Methyl groups are slowly oxidized and in combination with carboxyl, as in acetic acid or acetamide, are almost quantitatively stable, although carboxyls in themselves, as in formic, oxalic, and malonic acids, are easily oxidized. If acetic

acid is one of the products, it may be sufficiently stable for a quantitative procedure. For example, the odor of acetic acid is easily recognized during the oxidation of rhamnose, a methyl carbohydrate, and calculation taking this into account gives a yield of 102.0%. Ethyl alcohol, also, is oxidized within a few per cent of theoretical to acetic acid.

Methylene groups are less stable than CH_3 groups, and their presence in propionic, succinic, and malic acids apparently causes these substances to be less stable than acetic acid. However, the effect of CH_2 groups depends entirely upon neighboring groups, for, whereas malonic and citric acids are quantitatively oxidized, malic and succinic acids are resistant to considerably differing degrees, as are lauric and stearic acids.

The presence of an OH group apparently renders a carbon atom quantitatively oxidizable, as in the carbohydrates and glycerol, tartaric acid, inositol, and perhaps, most strikingly, glycolic (hydroxyacetic) acid. The difficultly oxidizable CH_3 group in methanol is rendered quantitatively oxidizable by the OH group. In this respect the CH_3O group, and the ether linkage, —C—O—C—, are apparently in the same category as the OH group, as shown by the results with methyl mannoside, methyl galacturonide, methyl galacturonide methyl ester, and trimethyl methyl mannoside. In fact, it appears possible to generalize that the presence of an oxygen atom of any type, alcohol, carbonyl, carboxyl, ester, and ether renders the particular carbon atom to which it is attached completely oxidizable to carbon dioxide. This general effect of oxygen seems to arise from a specifically engendered oxidizability, rather than merely an oxidative opening wedge, inasmuch as nitromethane, with a partially oxidized carbon atom, is not completely oxidizable to carbon dioxide by the present technique.

The effect of amino nitrogen, itself quantitatively nonoxidizable (*2*, *3*), varies greatly. Glycine is more oxidized by the reagent than acetic acid; serine is almost but definitely less than completely oxidized; nicotinic acid, which resembles benzoic acid except that it has nitrogen in place of the meta carbon atom, is, however, practically nonoxidizable. In other positions the NH_2 group has little or no effect, as in acetamide or anthranilic acid. The +3 nitrogen of *p*-nitrophenol was quantitatively oxidized to the +5 state by the reagent.

The aromatic ring as well as unsaturated structures like malic acid are completely oxidized, although the yields for the aromatics tend to be somewhat lower than those of the aliphatics.

CONCLUSIONS

The results indicate that organic substances whose carbon atoms are all individually attached to oxygen atoms, or aromatics, can be determined with small error in the presence of moisture, ash, and other nonoxidizables, or as pure components in a binary mixture, with the method described, assuming complete oxidation of carbon to carbon dioxide. On the other hand, substances reproducibly oxidized to carbon dioxide plus a fairly stable intermediatelike acetic acid can be approximately quantitatively determined by taking this product into account theoretically, or accurately by standardizing the reagent against the pure substance.

For samples with one oxidizable component, *A*:

$$\% A = \frac{V \times N}{a} \times 100$$

For samples with pure components *A* and *B*:

$$\% A = \frac{V \times N - b}{a - b} \times 100$$

where V = volume in liters of dichromate solution of normality N reduced per gram of actual weight of sample, and a and b = equivalents of dichromate reduced per gram of pure components A and B. These values are either theoretical ones deduced from formula or empirical ones determined by experiment, in accordance with the results presented in this paper.

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Rapid Accurate Determination of Cellulose with the Dichromate Heat-of-Dilution Method

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THE heat-of-dilution method for the determination of carbohydrates and certain types of other substances (*5*) is also applicable to celluloses. The α-cellulose determination is extensively used (*2*, *7*, *8*) in research and industrial control work on paper, rayon, wood pulps, and related products, and at least three standard (*1*, *10*) methods are in use in this country, whereas total cellulose is routinely determined in cotton (*3*). In most of these applications, speed and/or precision are essential, and many efforts have been made toward this end. This report presents comparable results with the heat-of-dilution method and another method requiring external heating, applied to identical samples of celluloses, starch, and glucose, with identical reagents.

METHOD

The heat-of-dilution method has been described (*5*). No attempt was made to dissolve the celluloses and precision oxidation was secured in the heterogeneous system. A 3-minute period after the addition of the acid was found to suffice for cellulose, starch, and glucose.

The method requiring external heating was essentially that used by Kettering and Conrad (*3*), in which 0.09 gram of cellulose, dry basis, is dissolved in 25 ml. of 12*M* sulfuric acid. Then 20 ml. of water and 10.00 ml. of 1.835*N* dichromate solution are added, and the mixture is boiled under reflux for 1 hour, and finally diluted and titrated as usual.

MATERIALS

The surgical cotton was a commercial product of unknown

origin and was used without purification. Ground (20-mesh) and unground specimens gave the same oxidimetric results.

The three samples of purified cellulose were prepared and contributed by C. M. Conrad, Southern Regional Research Laboratory, and were used without further treatment. The high- and low-viscosity celluloses were commercially purified and derived from cotton; the viscose rayon, from wood. The latter had been extracted with hot ethyl alcohol to remove resins, etc., at the Southernal Regional Research Laboratory. Moisture in the celluloses was determined with a vacuum oven at 3 mm. of mercury and 110° C. for 20 hours.

Ash was determined for all materials at 550° C. for 16 hours, after precharring with infrared. Ash values for the celluloses in the order of Table I were 0.04, 0.13, 0.02, and 0.05%.

The starch and glucose have been described (*5*).

RESULTS AND DISCUSSION

The results by the two methods on the celluloses, starch, and glucose are shown in Table I. The yield values were calculated as in previous work (*5*).

Of the sources of error previously discussed, only two need be stressed. Moisture in cellulose is particularly difficult to determine because the last traces of water are tenaciously retained by such high polymers. Both sets of values are probably too low, by the same amount, because of this effect. Nelson and Hulett (*6*) found by extrapolation to 250° C. that 0.41% water remained in their cellulose at equilibrium at 115° C. and 0.001 mm. of mercury. If such a value could be applied to the celluloses of Table I, the heat-of-dilution method could be assumed to give truly theoretical yields for celluloses. The high yield for surgical cotton would then have to be ascribed to oxidizable impurities of a more reduced nature than cellulose.

Table I. Comparison of Results by Two Methods on Celluloses, Starch, and Glucose

	Heat-of-Dilution Method			External Heating Method		
Substance	Yield, % of theory	Standard deviations	No. of replicates	Yield, % of theory	Standard deviations	No. of replicates
High viscosity cotton	99.70	0.18	6	98.50	0.24	6
Surgical cotton	100.05	0.27	12	98.20	0.08	4
Viscose rayon	99.65	0.12	6	98.50	0.24	6
Low viscosity cotton	99.60	0.21	16	98.45	0.18	8
Starch	99.35	0.21	10	98.25	0.22	8
Glucose	99.40	0.12	12	99.20	0.21	8

The other error is due to carbon monoxide formation and escape. Segal, Tripp, Tripp, and Conrad (*9*) have shown that 1.0 to 1.6% of glucose and cellulose was converted to carbon monoxide when they used the same method of external heating applied herein for comparison. They measured the amount of carbon monoxide which escaped from solution and thus accounted for their low results, which were in essential agreement with those in Table I, column 5, the glucose value of which fits into their range of values (their Table IV).

It appears reasonable to account for the difference between the two sets of yield values as being due to smaller quantities of carbon monoxide formed or escaping in the heat-of-dilution method. This could be the result of the much more rapid heating, together with the two- to fivefold greater concentrations of acid and dichromate in the present method over that of external heating. Furthermore, in the latter method, some oxidation, approximately 9%, occurs during the addition of dichromate to the cellulose solution. Since under these conditions cellulose is in excess a part of the time, carbon monoxide formation may be favored.

Both procedures are combined in the α-cellulose determination developed at the National Bureau of Standards (*4*) and used as ASTM and TAPPI standard methods (*1*, *10*). Solution of cellulose by 12*M* acid, followed by dichromate, is used in the alpha fraction, whereas addition of concentrated acid to the dichromate-cellulose mixture is used for the alkali-soluble fraction. The latter is thus oxidized through heat of dilution; subsequent external heating completes the oxidation of resins. Errors in the alkali-soluble fraction are the only critical ones; those in the alpha fraction cancel out, practically speaking, inasmuch as a 1.5% error therein would result in an error of only 0.1% in an α-cellulose value near 90%, as calculated from total cellulose.

CONCLUSION

Cellulose can be determined rapidly and with slight error, in the presence of moisture and usual inorganic impurities, by applying the theoretical factor 0.01240 gram of cellulose per ml. of 1.835 *N* (90.00 grams per liter) potassium dichromate solution, with the dichromate heat-of-dilution method.

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Infrared Determination of Total Aromatics

In Naphthas and Catalytic Reformates Boiling between 200° and 400° F.

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DETERMINATION of total aromatics in hydrocarbon fractions is of considerable interest to petroleum refiners, and has been the subject of many investigations. Methods have been developed through use of several techniques, including acid absorption (*1*, *5*), ultraviolet (*8*), Raman (*6*), mass spectrometry (*2*), and adsorption (*3*).

The infrared method was developed to overcome difficulties encountered in several of these techniques, and is found to provide a rapid, reasonably accurate analysis, with limitations, interference, and errors as discussed below.

APPARATUS AND MATERIALS

All spectra were obtained with a Perkin-Elmer Model 21 spectrometer, using rock salt cells and prism. The maker's recommended quantitative conditions were used throughout (*9*). Recordings were linear in wave length.

All pure compounds were obtained from the National Bureau of Standards and were of better than 99% purity, except *o-tert*-butyltoluene, which was obtained from the National Advisory Committee for Aeronautics, Washington, D. C., and was of unknown purity.

Table I. Values of K for Pure Compounds

(Area in square centimeters × molecular weight divided by 100)

Compound	Boiling Point, ° F.	K	Deviation from Extrapolated Average
Benzene	176	38.2	+11.1
Toluene	232	27.2	+0.1
Ethylbenzene	277	28.0	+0.9
o-Xylene	291	25.5	−1.6
m-Xylene	282	25.8	−1.3
p-Xylene	282	22.1	−5.0
o-Methylethylbenzene	323	26.3	−0.8
m-Methylethylbenzene	325	25.6	−1.5
p-Methylethylbenzene	323	22.5	−4.6
n-Propylbenzene	318	29.3	+2.2
Isopropylbenzene	305	28.8	+1.7
1,2,3-Trimethylbenzene	351	24.7	−2.4
1,2,4-Trimethylbenzene	338	23.0	−4.1
1,3,5-Trimethylbenzene	329	26.0	−1.1
n-Butylbenzene	356	29.4	+2.3
Isobutylbenzene	345	29.6	+2.5
sec-Butylbenzene	340	28.8	+1.7
tert-Butylbenzene	336	30.8	+3.7
o-Cymene	347	27.8	+0.7
m-Cymene	349	25.8	−1.3
p-Cymene	349	32.2	−3.9
1-Methyl-2-*n*-propylbenzene	360	Not available	
1-Methyl-3-*n*-propylbenzene	351	Not available	
1-Methyl-4-*n*-propylbenzene	363	Not available	
1,2,3,4-Tetramethylbenzene	399	Not available	
1,2,3,5-Tetramethylbenzene	387	22.6	−4.5
1,2,4,5-Tetramethylbenzene	383	27.2	+0.1
1,2-Dimethyl-3-ethylbenzene	381	Not available	
1,3-Dimethyl-2-ethylbenzene	374	Not available	
1,2-Dimethyl-4-ethylbenzene	374	Not available	
1,3-Dimethyl-4-ethylbenzene	371	Not available	
1,4-Dimethyl-2-ethylbenzene	368	Not available	
1,3-Dimethyl-5-ethylbenzene	363	26.4	−0.7
o-Diethylbenzene	363	26.1	−1.0
m-Diethylbenzene	358	25.8	−1.3
p-Diethylbenzene	360	21.1	−6.0
Indane	350	27.6	+0.5
o-*tert*-Butyltoluene	393	30.5	+3.4
m-*tert*-Butyltoluene	373	24.4	−2.7
p-*tert*-Butyltoluene	379	28.6	+1.5
Tetralin	405	30.2	+3.1
Average of all aromatics		26.3	−0.8
Extrapolated value		27.1	...
Value obtained by actual analysis		28.9	+1.8
Standard deviation by method of summation of squares			2.8
Relative standard deviation			10.4%
Standard error			0.55

DEFINITIONS AND SYMBOLS

A = area in square centimeters bounded by 5.00 microns, 100% transmittance, 5.85 microns, and the absorption curve

M = average molecular weight of the aromatics in a given sample, determined by mass spectrometry or other means

$K = AM/100$ for a theoretical 0.100-mm. cell

THEORY AND DEVELOPMENT OF METHOD

The measurement region is 5.00 to 5.85 microns, where absorption bands are probably due to overtones and combinations (*7*, *10*). No theoretical treatment is at present available. The relationships between substitution types and spectral patterns in the 5- to 6-micron region were first described by Young, DuVall, and Wright (*10*).

This method utilizes a value which is related to integrated intensity (*4*). The latter was not calculated, as measurements were made on a linear wave-length instrument, and convenient and reproducible "wing" measurements could not be made.

Initial attempts to develop a method by measurements of band absorbances and areas failed, because of the high specificity of the infrared method for substitution types. Inspection of the 6-micron region showed that the areas under the curves between 5 and 6 microns were fairly constant for a given molecular weight. Subsequent calibration proved the approximate constancy of K for aromatics in the 200° to 400° F. range. In order to minimize olefin interferences, the 5.85-micron value was arbitrarily selected as the boundary on the long wave-length side. "Background" effects were satisfactorily handled through use of a standard raffinate solvent, discussed later.

Molecular weight may be obtained by any suitable procedure, but in this work values were obtained by mass spectrometry (*2*).

At this time the authors are studying application of the method to higher boiling aromatics. Initial results indicate that extension is valid for mononuclear aromatics, as, for example, in the cases of C_{12}-C_{19} compounds, whose K's fall into the range shown in Table I. Biphenyls and naphthalenes have different K's, although for the limited number of compounds examined, each group is approximately constant as a class. In addition, a relationship may exist between classes. This is a subject of present investigation, but is not reported here because of insufficient data.

Table II. Composition of Aromatic Blend for Calibration

Compound	Weight %	Compound	Weight %
Toluene	6.27	Isobutylbenzene	1.15
Ethylbenzene	6.34	*n*-Propylbenzene	1.12
m-Xylene	6.36	1-Methyl-2-ethylbenzene	0.72
m-Methylethylbenzene	6.62	1,2,3-Trimethylbenzene	1.29
p-Methylethylbenzene	6.14	*n*-Butylbenzene	1.21
Isopropylbenzene	5.80	*sec*-Butylbenzene	1.21
1,2,4-Trimethylbenzene	6.48	*tert*-Butylbenzene	1.10
1,3,5-Trimethylbenzene	6.19	*p*-Diethylbenzene	1.02
m-Cymene	5.77	*m*-Diethylbenzene	1.20
p-Cymene	5.91	*o*-Diethylbenzene	1.28
1,2,3,5-Tetramethylbenzene	6.27	*o*-Cymene	1.17
1,3-Dimethyl-5-ethylbenzene	5.85	1-Methyl-3-*tert*-butylbenzene	1.19
Indane	7.64	1-Methyl-4-*tert*-butylbenzene	1.18
p-Xylene	1.19	1-Methyl-2-*tert*-butylbenzene	1.13
o-Xylene	1.18		

Analysis, %	Actual	Infrared	Ultraviolet
	100	98.1	96.7

Table III. Reproducibility of K by Repeated Analyses

Blend	Weight % Aromatics	Weight % Found in Run 1	2	3
AB-3	40.4	39.0	39.0	39.0
AB-5	61.7	59.5	59.6	59.8

Table IV. Total Aromatics in Blends of Corpus Christi Naphtha

Sample No.	Boiling Range, ° F.	Weight Per Cent Infrared	Ultraviolet	Acid absorption
1582	297–340	17.8	21.2	20.8
1583	340–375	25.1	21.8	24.5
1599	202–248	4.2	7.6	..
1600	248–297	13.2	18.1	...
1624	375–399	27.3	22.3	29.0

Table V. Total Aromatics in Cuts of Rangely, Colo., Crude

Cut No.	Boiling Range, ° F.	Weight Per Cent Infrared	Ultraviolet	Mass spec.	Acid absorption
2	207	0.0	1.0	...	...
3	215	3.0	5.9	...	...
4	232	5.8	6.4	...	...
5	243	0.0	1.3	...	...
6	251	0.0	0.6	...	...
7	260	1.0	4.3	...	...
8	271	16.3	13.6	...	...
9	280	14.3	17.6	...	...
10	292	3.4	8.0	...	...
11	300	0.3	3.7	...	...
12	311	7.0	8.3	...	...
13	320	14.0	15.9	...	...
14	331	15.0	18.0	...	...
15	341	14.3	15.5	...	...
16	349	10.7	13.3	...	...
17	161 (15 mm)	14.3	12.9	...	...
18	173 (15 mm)	14.8	13.6	...	...
Blend 2-18[a]	...	9.2	8.7	9.1	9.4

[a] Weighted average of individual cuts based on infrared shows 7.9 weight %.

CALIBRATION

Calibration was accomplished in several steps.

The 5- to 6-micron spectrogram was obtained for available aromatics in the 200° to 400° F. range. Areas within the previously described boundaries were measured in square centimeters with a compensating polar planimeter. Measurements were repeated, until three readings agreed within 0.1 sq. cm., and the average of these three was taken. Areas obtained were multiplied by molec-

Table VI. Total Aromatics in Reformates

Sample No.	Weight % Infra-red	Mass spec.	Acid absorption	Sample No.	Weight % by Infra-red	Mass spec.	Acid absorption
17007	4.4	3.4	16.6	28041	55.2	55.5	65.8
17035	6.5	7.3	12.0	28042	68.0	68.9	78.2
17082	64.0	60.0	72.0	28043	58.0	54.4	65.7
17084	62.0	56.6	69.5	28044	65.5	64.0	75.0
17021	4.0	4.4	8.8	28046	52.0	47.6	59.6
17024	5.0	5.3	7.4	28047	59.5	62.0	71.0
17029	21.6	19.9	27.5	28051	51.0	46.2	57.0
28031	51.5	45.9	57.5	28052	62.5	59.1	68.8
28032	58.0	57.3	66.0	28054	46.0	45.2	53.1
28034	51.5	46.4	57.8	28055	56.5	53.1	64.8
28035	78.0	79.1	71.6	28057	52.0	47.3	59.2
28039	71.7	82.9	87.0	28037	75.0	80.0	

Table VII. Total Aromatics in Synthetic Blends

Wt. % Added Aromatics[a] Present	Found	Deviation, %
49.7	48.5	−1.2
34.8	33.6	−1.2
26.9	28.2	+1.3
20.1	21.7	+1.6
10.8	12.9	+2.1

[a] Original contained 6.8 wt. % aromatics by infrared.

Table VIII. Errors Caused by Contamination

Contaminant	Theoretical Wt. % Aromatics	Wt. % Found	Deviation, %
1.65% benzene	67.2	70.0	+2.8
4.94% benzene	68.3	74.0	+5.7
0.51% naphthalenes	76.0	76.5	+0.5
1.76% naphthalenes	76.5	77.5	+1.0
5.0% olefins	76.0	76.5	+0.5
9.9% olefins	68.4	69.5	+1.1

ular weights and the product was corrected to give K for a theoretical 0.100-mm. cell. Values of K for pure compounds are listed in Table I.

A raffinate was prepared as described below, and a blend of available calibration samples was made, with composition shown in Table II. A series of blends of aromatics in raffinate was made, and their spectra were obtained. K was calculated and plotted against theoretical weight per cent aromatics, giving a straight line. The extrapolation to both ordinates gives reasonable agreement with calculated values (see Table I). Individual deviations are small, so that large changes in molecular distribution can be tolerated.

Two blends were run repeatedly under identical conditions to check reproducibility. Deviations are listed in Table III.

ANALYTICAL PROCEDURE

A sample is placed in a 0.108-mm. cell, and its spectrogram is obtained between 5.00 and 5.85 microns.

The area under the curve is measured, and K is calculated, using mass spectrometry for molecular weight.

Reference to the calibration curve gives weight per cent total aromatics directly. Time required for a single analysis is less than 30 minutes, including molecular weight determination.

APPLICATIONS TO PETROLEUM-BASED MATERIALS

Many determinations have been made by this method, and values were compared to those of other methods when possible. Table IV shows results from blends of Corpus Christi naphtha. Table V lists data for Rangely, Colo., naphtha. Table VI shows data for cuts of two different catalytic reformates. Mass spectrometer data were obtained by the method of Brown (*2*), with slight modification; ultraviolet data by the method of Kinder (*8*); and acid absorption data by ASTM method (*1*). Data by the LeTourneau method (*3*) were not available.

INTERFERENCES AND ERRORS

Interferences are generally of two types: (1) nonaromatics which absorb in the 5- to 6-micron region, such as carbonyls, olefins, thiophenes, and pyridine, and (2) aromatics whose K varies from the established values, such as benzene, naphthalene, and polyphenyls.

Obviously, the extent of the interference will vary with the absorptivity and concentration of the interfering compound. In practice, small amounts of olefins and naphthalenes do not interfere seriously. Many of the samples in Table VI were known to contain both.

A particular advantage of the method is that the identity of an interfering compound may often be established from the spectrogram and suitable correction made, based on its concentration and contribution to the area measurement.

Inspection of the data shows that indane and Tetralin (1,2,3,4-tetrahydronaphthalene) K's are within the general range. Although no substituted indanes and Tetralins were available, there is no apparent reason for nonconformity.

Errors based on deviations of single compounds from the average are computed and shown in Table I. These values indicate that the method is reliable. Errors based on deviations from Beer's law are negligible for concentrations between 10 and 95%, as shown by the straight line obtained. Errors based on synthetic blends are shown in Table VII, indicating a slight curvature to the calibration curve.

Errors caused by inclusion of typical impurities are shown for the cases of benzene, naphthalenes, and olefins in Table VIII. The naphthalene contaminant was composed of 17% naphthalene, 65% 1-methylnaphthalene, and 17% 2-methylnaphthalene. The olefin contaminant was a C_9-C_{10} cut of propylene polymer, and by infrared analysis contained a large proportion of terminal olefin. It is apparent from this that approximately 1% benzene, 2% naphthalenes, and 10% olefin can be tolerated.

RAFFINATE PREPARATION

A 200° to 400° F. fraction of a mid-continent crude was acid-treated, washed, dried, and percolated through silica gel, until it contained less than 0.005% total aromatics by ultraviolet absorption methods. A second raffinate was similarly prepared from a reformate.

Values of K deviated by less than the magnitude of analytical error anticipated, so that the first prepared raffinate was used throughout the calibration.

ACKNOWLEDGMENT

The author is grateful to the Sinclair Research Laboratories, Inc., for permission to publish this work, and takes this opportunity to express appreciation to James Neel for his capable assistance throughout, and to various other groups who cooperated.

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Improved Method of Determining Densities of Viscous Fluids with Babcock Bottles

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MANY types of pycnometers have been devised to measure densities (*1*, *4–7*). Although they are suitable for the purpose for which they are designed, they are difficult to manipulate when viscous fluids are involved owing to poor capillary flow, have poor precision due to nonreproducible seating of ground glass joints, or are time-consuming when determining coefficient of expansion because of the necessity of having to refill and reweigh the pycometer for each measuring temperature.

The method described below provides precise and rapid testing of viscous fluids at different temperatures. The pycnometers used (*2*, *3*) are Babcock milk test bottles (Cenco No. 24340 or equivalent). These bottles have a wide base, a neck with 0.02 ml. per graduation, and a volume of 1.6 ml. The over-all volume of the bottle is about 50 ml.

The Babcock bottles are relatively easy to fill with a pipet and can be loaded in an oven if fluids too viscous to flow at room temperature are encountered. These bottles are adapted to nonviscous as well as viscous fluids. Density-temperature data can be obtained over a wide range of temperatures (130° F. for many fluids) without a separate weighing for each determination. Only initial (tare) and final weighings, as well as neck readings at each temperature, are necessary.

PROCEDURE

Calibrate the bottles by the standard method (*1*); the neck as well as the bulb must be calibrated. Determine the volume of the bulb at three temperatures over at least a 100° F. range (the authors used 100°, 140°, and 180° F.) using National Bureau of Standards oil, Type N, or equivalent. Water may be used at the lower temperatures. If the thermal expansion of the bulb is not linear with temperature after a second set of determinations, discard the bottle (this has been encountered in only one bottle to date). The neck volume is independent of temperature within experimental error. To fill the bottles these laboratories use a 50-ml. pipet in which a glass efflux tube 3 mm. in outside diameter replaces the standard efflux tube. The size of the efflux tube is not reduced at the end.

After filling, cool the bottles to below the test temperature, and carefully clean the neck of any adhering test fluid with a lintless tissue. If more than one test temperature is employed, use the lowest one first, so that drainage errors are eliminated.

Make neck readings at 10-minute intervals until three consecutive identical values are obtained. This assures thermal equilibrium.

These laboratories use an analytical balance having a sensitivity of 0.0001 gram and a constant-temperature water bath with a precision of ±0.008° F. and an accuracy of 0.1° F.

A formula indicating the Babcock bottle constants has been developed, so that when the density is calculated at a known temperature, only values of neck reading and fluid weight are necessary:

$$d_t = \frac{W}{V_b + kt + nV_n}$$

where

d_t = density of fluid at t° F., grams per ml.
W = true weight in vacuo of fluid in bottle, grams
V_b = volume of bulb at 0° F. (extrapolated), ml.
t = temperature of fluid (same as temperature of constant-temperature bath), ° F.
k = temperature coefficient of bulb as determined by calibration, ml. per ° F.
V_n = volume of neck (temperature-independent within experimental error), ml. per division.
n = Babcock bottle neck reading (estimated to tenths of a graduation)

These laboratories have determined fluid densities with a standard deviation of ±0.0001 gram per ml. (±0.005%) using different bottles (see Table I). Precision is slightly better for any particular bottle. With care, a precision of ±0.0002 gram per ml. (±0.01%) can be obtained with fluid viscosities of 1000 to 2000 cp. and temperatures of 160° to 180° F. (see Table II). Densities obtained by the Babcock method with similar fluids have been checked with standard pycnometers with complete agreement in the third decimal place (1 part in 2000). The absolute accuracy is probably about ±0.05% because of the additional errors involved in calibration.

Table I. Density of a Fluid in Different Babcock Bottles[a]

Bottle No.	Density, G./Ml.
1	1.9245
2	1.9239
3	1.9246
4	1.9246
5	1.9245
6	1.9245
7	1.9241
	Av. 1.9244
Maximum dev. from mean	±0.0005
Average dev. from mean	±0.0002
Standard dev. from mean	±0.0001

[a] Viscosity of fluid equal to approximately 400 cp. at test temperature of 144.7° F.

Table II. Density of Viscous Fluids in Different Babcock Bottles

Fluid No.	Bottle No.	Density, G./Ml. 160.2° F.	179.8° F.
1[a]	3	1.9404[b]	1.9238
	4	1.9405[b]	1.9242
	8	1.9404[b]	1.9239
2[c]	3	1.9408	1.9249
	4	1.9410	1.9252
	5	1.9408	1.9249
3[c]	1	1.9425	1.9267
	6	1.9427	1.9271
	8	1.9426	1.9269
4[a]	5	1.9402	1.9241
	6	1.9402	1.9242
	8	1.9402	1.9242
5[a]	1	1.9399	1.9242
	3	1.9399	1.9239
	4	1.9400	1.9239
6[a]	1	1.9400	1.9239
	3	1.9399	1.9236
	4	1.9400	1.9239

[a] Viscosity at 160° F. approximately 1500 cp.
[b] Test temperature 160.1° F.
[c] Viscosity at 160° F. approximately 2000 cp.

Conclusions. For each set of triplicate determinations the maximum spread of values is ±0.0002 gram per ml. (±0.01%); any individual value may be considered to have this precision.

ACKNOWLEDGMENT

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CRYSTALLOGRAPHIC DATA

74. Hafnium Oxide, HfO_2 (Monoclinic)

Contributed by S. GELLER and E. CORENZWIT

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IN RESPONSE to a number of requests for a publication outlet for incomplete descriptions of crystallographic data, this monthly column is now being opened for the publication of such material. Two examples of partial descriptions are published this month: one, principally x-ray data and the other principally optical and morphological data.

Most of the data to be published will still be in the form of complete descriptions; however, because of the usefulness of partial descriptions it is believed that through this means a great deal of worth-while data can be made available.

Monoclinic hafnium oxide is not a new discovery. The compound was reported by the von Hevesy (*1*) in 1932. However, von Hevesy did not report the powder data nor could it be found in a rather extensive literature survey.

The hafnium oxide reported herein was made by direct combination of a very small amount of high purity hafnium (supplied by the Foote Mineral Co.) with oxygen at 1100° C. in a closed-end platinum-rhodium wound resistance furnace. The oxide thus formed was allowed to cool slowly (over a period of 16 hours) to room temperature. No change in phase occurred when this compound was reheated to 1400° C. in an induction furnace and quenched.

The monoclinic hafnium oxide is white. As expected, it is isomorphous with ZrO_2 (*2*), the lattice constants being very close to those of the latter compound. They are: $a = 5.12$, $b = 5.18$, $c = 5.25$ A., all within ± 0.02 A., and $\beta = 98 \pm 0.5°$. The space group is $P2_1/c$. With four molecules per unit cell, the calculated density is 10.3 grams per ml.

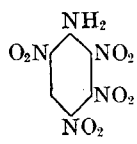
The powder diffraction photographs were taken with a North American Phillips powder camera of 114.6-mm. diameter using CuKα radiation. The data obtained are listed in Table I.

Table I. X-Ray Powder Diffraction Data for Monoclinic Hafnium Oxide

d, A. Obsd.	d, A. Calcd.	I/I_1	hkl	d, A., Obsd.	I/I_1
5.07	5.8	2	100	1.501	4
3.68	3.68	4	0.11	1.486	4
3.61	3.62	3	110	1.467	5
3.15	3.14	10+	11$\bar{1}$	1.439	3
2.82	2.82	10	111	1.410	5
2.59	2.59	6	002	1.352	2
	2.59		020	1.318	4
2.52	2.53	5	200	1.299	1
2.48	2.47	2	10$\bar{2}$	1.295	3
2.32	2.33	5	012	1.263	<1
	2.32		021	1.256	2
	2.30		120	1.237	<1
2.196	2.20	6	21$\bar{1}$	1.203	3
2.171	2.18	3	102	1.172	1
	2.16		12$\bar{1}$	1.160	1
2.006	2.01	3	112	1.153	1
1.981	1.98	4	211	1.143	1
	1.97		20$\bar{2}$	1.134	1
1.838	1.85	6	21$\bar{2}$	1.121	<1
	1.83		022	1.108	<1
1.807	1.81	6	220	1.099	1
1.794	1.79	2	12$\bar{2}$	1.084	1
1.768	1.77	3	22$\bar{1}$	1.070	<1
1.684	1.69	5	300	1.049	<1
	1.68		202	1.039	<1
1.653	1.65	6	221	1.025	1
1.634	1.64	4	013		
	1.64		0.31		
	1.63		11$\bar{3}$		
1.600	1.60	4	311		
	1.60		310		
	1.60		212		
1.580	1.58	3	13$\bar{1}$		
1.533	1.54	5	131		
	1.53		30$\bar{2}$		

75. 2,3,4,6-Tetranitroaniline

Contributed by W. C. McCRONE, Armour Research Foundation of Illinois Institute of Technology, Chicago 16, Ill.



Structural Formula of 2,3,4,6-Tetranitroaniline

CRYSTAL MORPHOLOGY

Crystal System. Monoclinic.

Form and Habit. Tablets lying on the basal pinacoid, {001}, showing the prism, {110}, and occasional faces of the bipyramid form, {111}.

Interfacial Angles (Polar). 110∧1̄10 = 118°.

Profile Angle. 95° (projection of 110∧1̄10 on 001).

Beta Angle. 146°.

Density. 1.76.

OPTICAL PROPERTIES

Refractive Indices (5893 A., 25° C.). $\alpha = 1.646 \pm 0.002$, $\beta = 1.775 \pm 0.005$, $\gamma = 2.22$ (calculated).

Optic Axial Angles (5893 A., 25° C.). $2V = 67° \pm 1°$ C.

Dispersion. Very strong inclined.

Optic Axial Plane. 010.

Sign of Double Refraction. Positive (>5650 A.), negative (>5650 A.).

Acute Bisectrix

Extinction (5893 A., 25° C.). $\gamma \wedge c = 21°$ in obtuse β.

Molecular Refraction (R) (5893 A.; 25° C.). $\sqrt[3]{\alpha\beta\gamma} = 1.86$. R(calcd.) = 55.4, R(obsd.) = 54.7 .

FUSION DATA. Crystals of 2,3,4,6-tetranitroaniline sublime readily to give yellow rhombs having a profile angle of 85° and a highly dispersed optic axis interference figure. On further heating the sublimate melts with decomposition at 210° C. The melt

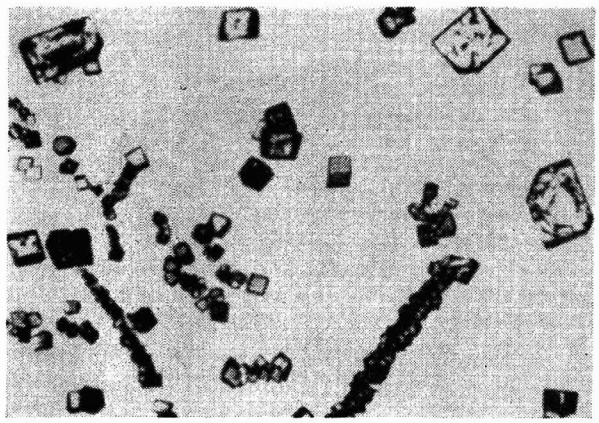


Figure 1. Crystals of 2,3,4,6-Tetranitroaniline from Molecule on a Microscope Slide

solidifies spontaneously to give thin crystalline films with extremely anomalous polarization colors.

ACKNOWLEDGMENT

Much of the work on tetranitroaniline was performed under contract between Cornell University and the Office of Scientific Research and Development during World War II. Alfred T. Blomquist was technical representative of OSRD Section B-2-A supervising this work. Sien-Moo Tsang and John A. Andreen were also associated with this project and contributed to the above description.

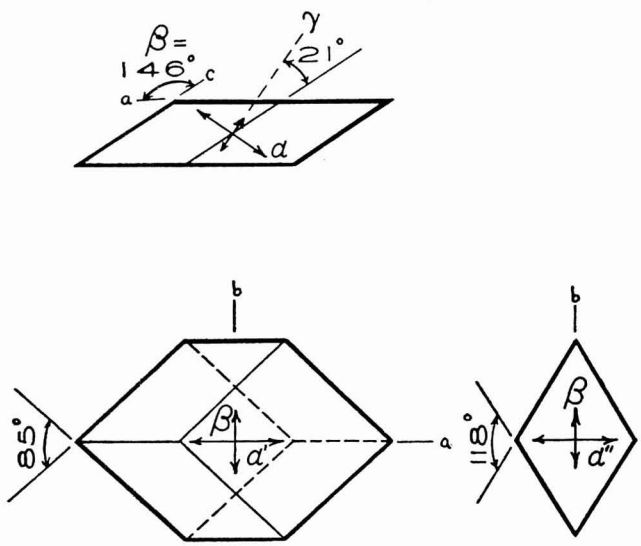


Figure 2. Orthographic Projection of Typical Crystal of 2,3,4,6-Tetranitroaniline

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CONTRIBUTIONS of crystallographic data for this section should be sent to Walter C. McCrone, Analytical Section, Armour Research Foundation of Illinois Institute of Technology, Chicago 16, Ill.

Correspondence

Modification of Parnas-Wagner-Pregl Micro-Kjeldahl Apparatus

SIR: Since publication of our "Modification of Parnas-Wagner-Pregl Micro-Kjeldahl Apparatus" [ANAL. CHEM., **25**, 535 (1953)], our attention has been called to a somewhat similar apparatus described by F. Rappaport [*Mikrochemie*, **14**, 49–74 (1933)]. While Rappaport also has a water inlet on the steam generator, there is a basic difference. This inlet is used only for the purpose of refilling the steam generator when empty. The advantages are that there is no need of refilling, the water used is ammonia-free (there is a Permutit column in the line), and it keeps the workbench clean. In our modification the steam generator is refilled slightly at the end of each distillation and this same addition of cold water is put to use by creating the partial vacuum necessary to draw the spent sample out of the distilling flask.

EDWARD H. SHEERS
MORTON S. COLE

Oldrich Tomicek

Oldrich Tomicek, professor of analytical chemistry at Charles University, Prague, Czechoslovakia, died October 21 at the age of 62 after a brief illness. Tomicek's name is well known to analytical chemists because of his many contributions to potentiometry, titrations in nonaqueous solutions, and indicators. He has published several books on analytical chemistry, including "Chemical Indicators," which appeared two years ago. He had been a member of the AMERICAN CHEMICAL SOCIETY since 1924.

Picrates of Alkylpyridines—Correction

The article "Picrates of Alkylpyridines Identification by X-Ray Diffraction Powder Patterns" [Janz, G. J., and Solomon, Raymond, ANAL. CHEM., **25**, 454 (1953)] illustrates the applicability of the powder diffraction method to the identification of these compounds, but the data cannot be used, as originally intended, as standards of reference for this purpose. Subsequent work has established that the target of the chromium tube used suffered contamination with tungsten and iron. Thus rather than monochromatic Cr-K_{α_1} radiation, the spectrum contained, in addition the Cr-K_{β_1}, Fe-K_{α_1}, K_{β_1}, and W-L_{α_1}, L_{β_1}, L_{β_2} lines. The powder patterns contained many extraneous lines leading to erroneous values for the interplanar spacings, and relative intensities. While these data can readily be corrected for the erroneous d spacings using the graphical method reported by Janz and Carroll (ANAL. CHEM., in press), it is not possible to correct the relative intensities of the lines. Further work, using pure Cr-K_{α_1}, or Cu-K_{α_1} radiation is necessary if data for use as absolute reference standards for the alkyl pyridine picrates is desired.

GEORGE J. JANZ
Department of Chemistry
Rensselaer Polytechnic Institute
Troy, N. Y.

BOOK REVIEWS

Organic Analysis. Edited by *J. Mitchell, Jr., I. M. Kolthoff, E. S. Proskauer,* and *A. Weissberger.* Vol. I. Interscience Publishers, Inc., 250 Fifth Ave., New York 1, N. Y. Price, $8.50.

"Organic Analysis," Vol. I, covers a portion of the functional group aspect of organic analysis (hydroxyl, alkoxyl, epoxy, active hydrogen, carbonyl, acetals, and spectroscopic functional group analysis in the petroleum industry). The remainder of the functional group aspect, along with other branches of organic analysis, will be covered in subsequent volumes.

The sections on the various groups deal mainly with chemical approaches, though at the end of each chapter there is usually a small section listing the instrumental methods which are available, as well as some chromatographic techniques which are used in conjunction with analysis of the group under discussion.

The book is encyclopedic in nature, each section being written by a different man who is well known in the particular field under discussion. Much historical work is mentioned (1056 references), and details are given for carrying out the recommended procedures.

This volume is an excellent reference book for the determination of the various groups discussed. The completed series on "Organic Analysis" should make a very good catalog of the information available in the field of organic analysis.

SIDNEY SIGGIA

Quantitative Anorganische Analyse in der Technik. *F. Specht.* 236 pages. Verlag Chemie G.m.b.H., Weinheim/Bergstr., Germany, 1953. Price, 1780 DM.

The author has compiled in book form numerous quantitative methods and techniques gathered during the course of 25 years as an inorganic analyst in Germany's heavy chemical industry. This work is not intended as a student text, but rather is considered useful as a laboratory manual and/or reference book.

The introduction discusses sampling methods for solids, liquids, and gases and the problems inherent in the sampling of inhomogeneous materials. The chapters that follow describe in detail the experimental procedures for the routine analysis of the raw materials, intermediates, and finished products most frequently encountered in inorganic chemical production. Many of these procedures are suitable for on-the-spot plant process control. The conclusion contains a description of the required glass apparatus and the usual standard solution preparation.

The experimental procedures are preceded by a discussion of their scope, applicability, and limitations. While the methods are almost entirely chemical in nature, some utilize electrolytic and spectrophotometric techniques. This book should be useful in the industrial inorganic control laboratory.

HANS J. STOLTEN

New Journal on Polarography

A new periodical in the German language dealing with polarography made its appearance in October 1952, with the first issue of *Leybold Polarographische Berichte,* a quarterly edited by Willi Hans and Hans Ulrich Bergmeyer, and published by Staufens Verlag, Cologne, Germany. Each volume will contain abstracts of articles on polarography—apparatus, methods, inorganic constituents, organic constituents, and theory—book reviews, questions and answers, and original contributions. Subscription price is DM 10, plus postage.

Cooperative Study of Student Accuracy in Quantitative Analysis

A COOPERATIVE study of student accuracy in quantitative analysis was organized at the Workshop in Analytical Chemistry held at Pennsylvania State College in June 1953. The study, which is about to be started, should answer the question of whether a given teacher's students do as well or as poorly as students in other schools in the analysis of unknowns and give data on the reliability of commercially available unknowns as a basis for grading students. Fourteen types of unknowns will be studied.

1. Soda Ash. Sister Eleanor Marie, Chestnut Hill College, Philadelphia, Pa.
2. Gravimetric Sulfate. John W. Schempf, Pennsylvania State College, State College, Pa.
3. Gravimetric Chloride. G. F. Hutchinson, Fairfield University, Fairfield, Conn.
4. Volumetric Chloride. W. P. Cortelyou, Roosevelt College, Chicago 5, Ill.
5. Potassium Acid Phthalate. Geo. H. Spaulding, Morgan State College, Baltimore, Md.
6. Volumetric Iron Ore. Lyle J. Michael, Otterbein College, Westerville, Ohio.
7. Volumetric Copper. Leslie V. Morris, Nashville Agricultural and Normal Institute, Madison College, Tenn.
8. Gravimetric Iron. Lillian Weidenhammer, Wilson College, Chambersburg, Pa.
9. Nitrogen in Blood. Thomas R. Sweet, Ohio State University, Columbus, Ohio.
10. Brass (Sn, Pb, Cu, Zn). Edward L. Haenisch, Wabash College, Crawfordsville, Ind.
11. Calcium Oxide in Calcium Carbonate ($KMnO_4$). John R. Hayes, Pennsylvania State College, State College, Pa.
12. Limestone (Ignition, SiO_2, R_2O_3, CaO, MgO). M. Gertrude McKeon, Connecticut College for Women, New London, Conn.
13. Manganese in Steel. Homer C. Imes, Rochester Institute of Technology, Rochester, N. Y.
14. Silver in a Silver Alloy. John D. Charlton, Wilmington College, Wilmington, N. C.

Any teacher who wishes to take part in the survey by submitting his records should write directly to the collector listed for standard report forms (one for each laboratory section to be reported). The collector will accept reports on from one to four laboratory sections in each participating school. Later each participating teacher will receive a summary of the accuracy achieved by students in the various schools, classified by type of school.

X-Ray Diffraction School

In order to supply educational information on the use and application of new instrumentation in the field of x-ray analysis, North American Philips Co., Inc., 750 South Fulton Ave., Mount Vernon, N. Y., established an x-ray diffraction school in 1946. Two days are devoted to lectures, laboratory work, and question and answer sessions on the basic principles of x-ray diffraction, and three days are devoted to x-ray diffraction applications. The most recent session was held October 5 to 9, and the next session is scheduled for April 1954.

The Analyst's Calendar

Metropolitan Microchemical Society

THE 1953–54 program of the Metropolitan Microchemical Society opened October 15 with a visit to the Calco Chemical Division, American Cyanamid Co., Bound Brook, N. J., which included a talk by Thomas Rees on "Micromethods for Measuring Reaction Rates in Solution under Moderate Pressure." Meetings are ordinarily held at the American Museum of Natural History, New York, N. Y. Secretary of the society is Geo. J. Hilsdorf, S.J., St. Peter's College, Jersey City, N. J.

November 19

Microscopic Identification of Organic Compounds. JOHN R. MITCHELL, Polychemicals Department, E. I. du Pont de Nemours & Co., Inc.
Motion picture of Kofler hot stage apparatus

December 17

Panel Discussions on Halogen Determinations

Amperometric Determinations. WILLIAM J. MADER, Merck & Co., Inc.
Carius Determinations. JOSEPH GRODSKY, Ortho Research Foundation
Statistical Survey of Halogen Determinations. MARIE W. GARNER, Hoffmann-La Roche, Inc.

January 21

Polarography of Organic Compounds. PHILIP J. ELVING, University of Michigan

February 18

Cathode Reduction of Surface Films. W. E. CAMPBELL, Bell Telephone Co.

March 19 and 20

Ninth Annual Microchemical Symposium, Brooklyn College
Standardization of Microchemical Apparatus and Methods

April 15

Authors Meet the Critics. AL STEYERMARK, Hoffmann-La Roche, Inc., NICHOLAS D. CHERONIS, Brooklyn College, A. A. BENEDETTI-PICHLER, Queens College

May 20

Ladies' Night, Fordham University

Ceramic Archeology. F. R. MATSON, Pennsylvania State College

Regional Conclave

THE Regional Conclave of the AMERICAN CHEMICAL SOCIETY will be held December 10 to 12 at New Orleans, La., with headquarters in the Jung Hotel. For the first time the southeastern and the southwestern sections of the Society are to meet together for a program with 202 papers in the fields of analytical chemistry, biochemistry, chemical education, organic chemistry, petroleum and chemical engineering, and physical and inorganic chemistry. Laboratory supply houses, apparatus and equipment manufacturers, and chemical companies will have exhibits in the headquarters hotel.

Symposia are planned in petroleum, spectroscopy, biochemistry, and chemistry of terpenes. No plant tours are scheduled during the conclave, but visitors are urged to come early or stay over to visit educational institutions, research organizations, and industrial plants. James A. Kime is Publicity Chairman of the Conclave Committee, 2100 Robert E. Lee Blvd., New Orleans, La. Fifty-one papers on analytical chemistry are scheduled.

Thursday Afternoon, December 10

H. P. BENNETT, *Presiding*

1:00 **Introductory Remarks.**
1:05 **Volumetric Determination of Sulfate.** JAMES L. KASSNER, ESTELLE O. JACKSON, AND MYRON E. CALKINS, University of Alabama, University, Ala.
1:15 **Titration Studies of Some Allyl Polyquaternary Ammonium Compounds.** WILLIAM J. HUSA, JR., AND ARMIN H. GROPP, University of Florida, Gainesville, Fla.
1:30 **Volumetric Determination of Alumina in Bayer Process Liquors.** ROBERT R. PHILLIPS AND ALTON E. MCLAUGHLIN, Kaiser Aluminum and Chemical Corp., Baton Rouge, La.
1:45 **Determination of Epoxides with Sodium Sulfite.** J. DONALD SWAN, Jefferson Chemical Co., Austin, Tex.
2:00 **Determination of Oxygen in Purified Argon, Carbon Dioxide, Helium, Hydrogen, and Nitrogen. Improved Winkler Method.** WANDA BRADSHAW AND LOUIS SILVERMAN, North American Aviation Co., Downey, Calif.
2:15 ***N*-Bromosuccinimide as an Organic Classification Reagent.** PAUL F. KRUSE, JR., AND THOMAS A. MCCOY, The Samuel Roberts Noble Foundation, Ardmore, Okla.
2:30 **Analytical Studies of Some Acyloin Oximes.** HANS A. SUTER AND PHILIP W. WEST, Louisiana State University, Baton Rouge, La.
3:00 **Microscopic Fusion Study of 2,4,5-Trichlorophenoxyacetic Acid and Related Compounds.** CLAUDE J. ARCENEAUX, Ethyl Corp., Baton Rouge, La.
3:30 **Theory of Electrolysis at Controlled Current in Unstirred Solutions. Experimental Study of Potential-Time Curves.** PAUL DELAHAY AND CALVIN C. MATTAX, Louisiana State University, Baton Rouge, La.
3:50 **Determination of Moisture in Salts by the High Frequency Method.** FRED W. JENSEN AND M. B. BURTON, JR., A. & M. College of Texas, College Station, Tex.
4:05 **Determination of Water in Alcohols by an Indirect Conductivity Method.** C. KINNEY HANCOCK, CHARLES M. HUDGINS, JR., AND RALPH E. ZERWEKH, JR., Texas Engineering Experiment Station, College Station, Tex.
4:25 **Acetic Anhydride in Nonaqueous Titrimetry and Its Role in the Determination of Sulfuric Acid Catalyst in Ethanol Esterification Mixtures.** A. F. GREMILLION, Carbide & Carbon Chemicals Co., Texas City, Tex.
4:40 **Coordination of Instrumental Analysis with Other Analysis Methods.** JOHN T. WILEY, The Texas Co., Port Arthur, Tex.
4:55 **Apparatus for the Determination of Sulfur in Petroleum Products by the Lamp Method.** HOWARD HOPKINS, Pawhuska Research Laboratory, Pawhuska Okla.

Thursday Afternoon, December 10

Symposium on Application of Spectroscopy to the Agriculture and Industry of the South

R. T. O'CONNOR, *Presiding*

1:00 **Introductory Remarks**
1:05 **Spectroisotopy. Applications of High Resolution Spectroscopy.** J. RAND MCNALLY, JR., Oak Ridge National Laboratory, Oak Ridge, Tenn.
1:35 **Mass Spectroscopy.** B. W. THOMAS, Humble Oil & Refining Co., Baytown, Tex.
2:05 **Emission Spectroscopy.** E. E. CREITZ, U. S. Bureau of Mines, University, Ala.
2:35 **Raman Spectroscopy.** FORREST F. CLEVELAND, Illinois Institute of Technology, Chicago, Ill.
3:05 **The X-Ray Spectrograph and Its Practical Uses.** FRED A. BEHR, North American Philips Co., Inc., Mt. Vernon, N. Y.
3:35 **Nuclear Magnetic Resonance Spectroscopy.** JAMES N. SHOOLERY, Varian Associates, Palo Alto, Calif.
4:05 **Infrared Spectrophotometry.** R. C. GORE, American Cyanamid Co., Stamford, Conn.
4:35 **Ultraviolet Spectroscopy.** NORMAN D. COGGESHALL, Gulf Research and Development Co., Pittsburgh, Pa.

Friday Morning, December 11

Radiochemistry. Joint with Inorganic and Organic

R. B. ESCUE, *Presiding*

9:00 **Introductory Remarks**

9:05 **Radioactive Tracers as Adsorption Indicators.** R. B. Escue and Newman P. Bulloch, North Texas State College, Denton, Tex.

9:15 **Use of Nuclear Techniques in Analytical Chemistry.** G. W. Leddicotte and S. A. Reynolds, Oak Ridge National Laboratory, Oak Ridge, Tenn.

9:40 **Determination of Trace Elements in Crude Oils and Distillation Products by Radioactivation Analysis.** G. W. Leddicotte and H. A. Mahlman, Oak Ridge National Laboratory, Oak Ridge, Tenn.

9:55 **Determination of Trace Elements in Grass and Grain by Radioactivation Analysis.** H. A. Mahlman and G. W. Leddicotte, Oak Ridge National Laboratory, Oak Ridge, Tenn.

10:10 **Isotope Effect Study of the Pinacol Rearrangement.** Wayne Carrick and Arthur Fry, University of Arkansas, Fayetteville, Ark.

10:20 **Use of Carbon-14 in a Competitive Reaction Rate Study.** Charles T. Lester and Gus A. Ropp, Oak Ridge National Laboratory, Oak Ridge, Tenn.

10:40 **Synthesis of 1,2-Dihydro-3,6-pyridazinedione-3,6-C^{14}.** J. Gray Dinwiddie, Jr., and John A. Porter, The Clemson Agricultural College, Clemson, S. C.

10:50 **One-Step Preparation of C^{14}-Cyanide from Barium Carbonate-C^{14}.** J. K. Jeanes, Texas Research Foundation, Renner, Tex.

11:00 **Electromagnetic Isotope Separation of the Palladium, Platinum, and Rare Earth Elements.** C. P. Keim, Oak Ridge National Laboratory, Oak Ridge, Tenn.

11:15 **Determination of Tritium by Radioautography.** D. E. Beischer, U. S. Naval School of Aviation Medicine, Pensacola, Fla.

11:30 **Gamma-Ray Spectroscopy in Analytical Radiochemistry.** Bernd Kahn and W. S. Lyon, Oak Ridge National Laboratory, Oak Ridge, Tenn.

11:40 **Causes for Abnormal Mass 30 Values in Nitrogen Isotope Analyses with the Mass Spectrometer.** Robert L. Ory, J. M. Prescott, and C. M. Lyman, Texas Agricultural Experiment Station, College Station, Tex.

Friday Afternoon, December 11

C. T. Kenner, *Presiding*

2:00 **Introductory Remarks**

2:05 **Composition of the Basic Ferric Formate Precipitate. Effect of Final pH.** C. T. Kenner, Southern Methodist University, Dallas, Tex.

2:20 **Principles of Precision Colorimetry. Two New Methods.** Charles N. Reilley, University of North Carolina, Chapel Hill, N. C.

2:35 **Effects of Time and Temperature on the Reaction of Formaldehyde with a Modified Schiff's Reagent.** Richard Hatfield and E. C. Smith, Southwest Research Institute, San Antonio, Tex.

2:50 **Colorimetric Determination of Small Amounts of Uranium in the Presence of Bismuth. Pentaether Thiocyanate Method.** Lavada Moudy and Louis Silverman, North American Aivation Inc., Downey, Calif.

3:05 **Determination of Low Hydrogen Cyanide in Acrylonitrile.** Robert L. Maute and M. L. Owens, Jr., Monsanto Chemical Co., Texas City, Tex.

3:20 **Determination of Free Gossypol in Mixed Feeds.** R. W. Storherr and K. T. Holley, Georgia Agricultural Experiment Station, Experiment, Ga.

3:45 **Photometric Titrations in Nonaqueous Solvents.** Charles N. Reilley and Barbara Schweizer, University of North Carolina, Chapel Hill, N. C.

4:00 **Spectrophotometric Determination of Copper After Solvent Extraction of the Copper-Pyridine-Thiocyanate.** Stephen S. Baird, University of Texas, Austin, Tex., and David W. Sanshuck, Naval Powder Factory.

4:20 **Influence of the Perrhenate Ion, ReO_4^-, on the Flame Photometric Determination of Potassium.** A. D. Melaven and A. J. Chadwell, University of Tennessee, Knoxville, Tenn.

4:35 **Flame Photometric Determination of Calcium and Magnesium.** Florence B. Strohmeyer, Byron E. Leach, and Robert G. Heath, Tulane University, New Orleans, La.

4:50 **Effects of Certain Alkali Compounds in the Burning of Powdered Graphite Samples.** E. L. Grove and J. A. Norris, Oak Ridge National Laboratory, Oak Ridge, Tenn.

Saturday Morning, December 12

C. L. Hoffpauir, *Presiding*

9:00 **Introductory Remarks**

9:05 **Polarographic Determination of Vanadium and Molybdenum in the Presence of Ethylenediaminetetraacetic Acid.** Robert D. Feltham and Ernest L. Martin, University of New Mexico, Albuquerque, N. M.

9:20 **High Frequency Measurements as Applied to Titrimetry.** H. W. Hamme, E. L. Grove, and J. L. Kassner, University of Alabama, University, Ala.

9:40 **Preliminary Studies of the Separation and Determination of Bismuth, Antimony, and Tin by Controlled Cathode Electroanalysis.** John A. Dean and S. A. Reynolds, University of Tennessee, Knoxville, Tenn., and Oak Ridge National Laboratory, Oak Ridge, Tenn.

10:05 **Peak Volume-Concentration Concept in Organic Acid Chromatography Using Progressively Changing Solvents.** Charles Mader, Oklahoma A. & M. College, Stillwater, Okla.

10:20 **Chromatographic Fractionation of Wood Carbohydrates.** Robert Roy Bridges, Masonite Corp., Laurel, Miss.

10:35 **Analysis by Alumina Adsorption of the Aromatics Boiling above 400° F. in Jet Fuels.** C. M. McKinney and R. L. Hopkins, U. S. Bureau of Mines, Bartlesville, Okla.

Other papers of interest to analytical chemists include the Symposium on Physicochemical Methods in Biochemistry on Friday afternoon, and papers on chemical education on Friday afternoon and Saturday morning.

Conference on Defects in Crystalline Solids

The H. H. Wills Physical Laboratory, University of Bristol, in cooperation with the International Union of Pure and Applied Physics, particularly its Commission for the Physics of the Solid State, and with the Institute of Physics, is organizing a conference on defects in crystalline solids to be held July 13 to 17, 1954, in Bristol. Particular attention is to be given to defects such as dissolved atoms, vacancies and *F*-centers, microwave resonance methods of investigating their properties, and the way in which they react with dislocations. Further information is available from the Secretary, H. H. Wills Physical Laboratory, Royal Fort, Bristol 8, England, or the Secretary, Institute of Physics, 47 Belgrave Square, London S.W. 1, England.

Michigan Instrumentation Symposium

A Symposium on Instrumentation, sponsored by the Scientific Apparatus Makers Association, American Industrial Hygiene Association, American Conference of Governmental Industrial Hygienists, and the Institute of Industrial Health and School of Public Health of the University of Michigan, will be held at the University of Michigan, Ann Arbor, Mich., May 24 to 27, 1954. The program will include exhibits, discussions, and technical papers on instrumentation. It is planned to publish the papers in an illustrated book which will include technical data supplied by the instrument makers. Information is available from Director, Continued Education, School of Public Health, University of Michigan, Ann Arbor, Mich.

Metropolitan Microchemical Society. American Museum of Natural History, New York, N. Y. November 19 and December 17

Regional Conclave, American Chemical Society. New Orleans, La., December 10 to 12

American Chemical Society. 125th National Meeting, Kansas City, Mo., March 24 to April 1, 1954

Symposium on Instrumentation. University of Michigan, Ann Arbor, Mich., May 24 to 27, 1954

AIDS FOR THE ANALYST . . . .

Circular Slide Rule for Microanalysts. Ralph E. Schachat[1] and Walter L. Savell, Laboratory of Advanced Research, Remington Rand, Inc., South Norwalk, Conn.

THOMPSON [Thompson, R. C., ANAL. CHEM., 25, 535 (1953)] recently discussed the advantages of choosing a definite weight of sample for a carbon-hydrogen determination rather than a random quantity. She described the construction of a linear instrument that permitted the analyst to compute quickly the optimum weight of sample for the probable carbon and hydrogen content.

The instrument described here is simple in construction and operation. In addition, by means of extra scales, the computation of optimum weight of sample for a Dumas nitrogen analysis is made possible. The instrument can also be used as a conventional circular slide rule, enabling the operator to multiply, divide, and determine reciprocals. Other scales, such as square root, cube root, log log, etc., may be added if desired.

THEORY

The symbols used in calculating the layout of the scales and sliders are as follows:

θ = angle in degrees from the starting point or "index" for any value of X
θ_C = angle between the dotted line of the carbon slider and the carbon content–indicating arrow
θ_H = angle between the dotted line of the hydrogen slider and the hydrogen content–indicating arrow
θ_R = open area angle on the carbon slider between the broken and solid line. The solid line is referred to as the "indicator line" for multiplying and dividing operations.
θ_S = open area angle on the hydrogen slider between the broken and solid line
θ_N^1 = angle between the nitrogen-indicating arrow and the 1-ml. selector
$\theta_N^{0.5}$ = angle between the nitrogen-indicating arrow and the 0.5-ml. selector
X = any number between 0 and 100

The instrument consists of five parts, shown in the accompanying figures. Figures 1 and 2 represent the arrangement of the two sides of the slide rule, where the inner scale refers to the theoretical per cent of the element sought and the outer scale refers to the optimum sample weight in milligrams. All the scales are based on the formula $\theta = 180 \log_{10} X$ so that each 360° scale is actually composed of a regular linear slide rule scale arranged so that the numbers 1 to 10 extend from 0° to 180° and numbers 10 to 100 extend from 180° to 360°. The reason for choosing the numerical range of 1 to 100 for the inner scale is that 1 to 100 includes all possible percentages of carbon, hydrogen, and nitrogen found in organic compounds (except for a very few isolated cases).

[1] Present address, Central Laboratories, General Foods Corp., 1125 Hudson St., Hoboken, N. J.

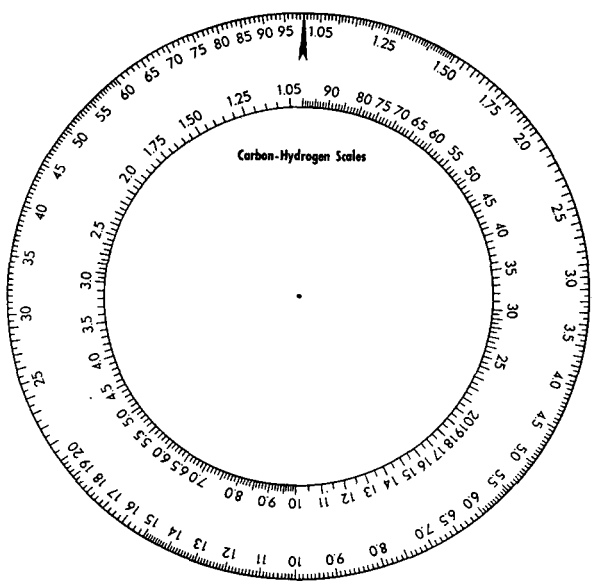


Figure 1. Carbon-Hydrogen Scales

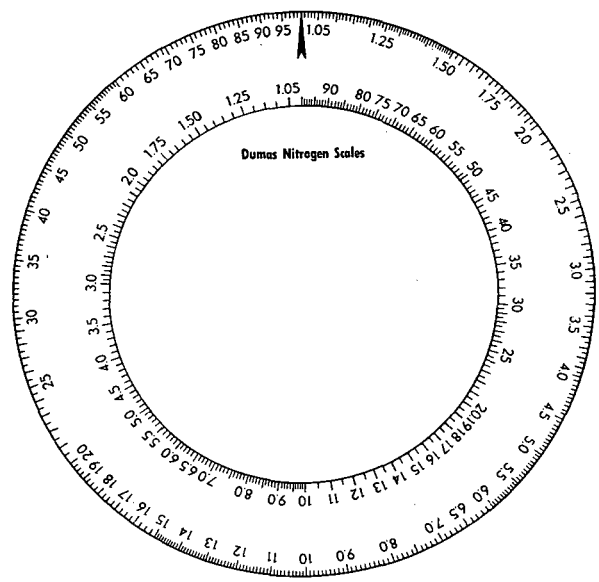


Figure 2. Dumas-Nitrogen Scales

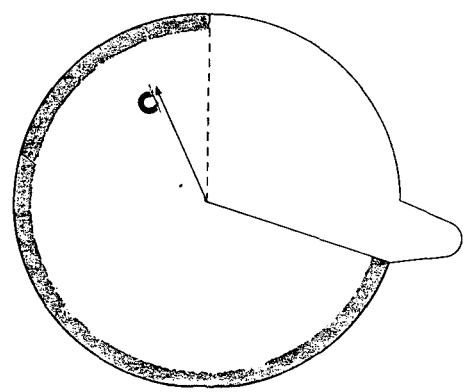


Figure 3. Carbon Slider

Scale up to same size as Figure 1

The range 1 to 100 was chosen for the outer scale because this range in milligrams includes all likely sample weights. As an additional advantage, keeping the same range for both scales allows reciprocals to be conveniently determined (see Use of Rule). The two scales on one side start at the same point, but run in opposite directions.

The "open area" angle on the C slider (Figure 3) and H slider (Figure 4) is obtained as follows: The optimum weight of carbon dioxide obtained may be considered to be 5 to 20 mg. (1 to 4 ratio), while optimum of weight of water is 2.5 to 10 mg. (also 1 to 4 ratio). Therefore, the angle will be $\theta_R = \theta_S = 180 \log_{10} (4/1) = 108.4°$ for both the C and H sliders.

The positions of the indicator arrows are computed as follows: Each milligram of hydrogen in the compound produces about 9 mg. of water. Therefore, $\theta_H = 180 \log_{10} (2.5/9) = -100.2°$, the angle between the broken line of the H interval indicator and the H arrow. Similarly, $\theta_C = 180 \log_{10} 5/(44/12) = 24.0°$.

The form of the nitrogen indicator (Figure 5) is calculated as follows: At 25° C. (approximately room temperature) and 1-atmosphere pressure, 1 ml. of nitrogen weighs 1.1457 mg. Therefore, $\theta_N^1 = 180 \log_{10} (1.1457) = 10.6°$. A 0.5-ml. selector (dotted line) is also included; its angle ($\theta_N^{0.5}$) is calculated in the same manner. Since 0.5 ml. of nitrogen at 1-atmosphere pressure and 25° weighs 0.5729 mg., $\theta_N^{0.5} = 180 \log_{10} (0.5729) = -43.6°$.

For the analyst who prefers other volumes of nitrogen, other indicating lines can be constructed in an analogous manner. Alternatively, the slider can be divided into segments that will show the sample weight range for any desired volume range.

CONSTRUCTION OF RULE

The scales and sliders were computed by use of the θ values as described under Theory. A small arrow or "index position" indicated the starting point of the outer scale. Actual construction of a workable rule consisted of pasting the carbon-hydrogen scale (Figure 1) on one side of a piece of stiff cardboard and the nitrogen scale (Figure 2) on the other. The three sliders were traced onto stiff plastic and scaled up to the same size as the scales of Figures 1 and 2. Thus, the length of the arrows was made equal to the radius of the inner circle of the scales. The length

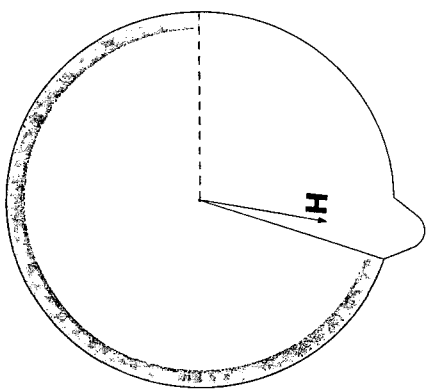


Figure 4. Hydrogen Slider

Scale up to same size as Figure 1

of the solid and broken lines and, hence, the radius of the outer circle of the slider was made equal to the radius of the outermost circle of the scales. The indicated area on the carbon slider was colored yellow by masking the uncolored area and then spraying the exposed portion with transparent waterproof ink from an air brush. Similarly, the indicated portion of the hydrogen slider was colored blue. The width of the colored band was sufficient to cover the outermost series of numbers. No coloring was used on the nitrogen slider. Holes were punched with a cork borer in the exact center of the scales and sliders. The apparatus was assembled with a loose-fitting rivet with the sliders face up on the appropriate side of the scales; the carbon indicator was placed under the hydrogen indicator.

USE OF RULE

For Carbon and Hydrogen Determinations. Point the C arrow at the theoretical per cent carbon and the H arrow at the theoretical per cent hydrogen (inner scale). The clear area between the yellow and the blue fields on the outer scale will then indicate the optimum range of sample weight in milligrams. For the few cases in which there is no clear area, the optimum sample range is indicated by the doubly covered (green) part of the scale. As there will be two green areas, choose the one most distant from the index position of the scale.

For Dumas Nitrogen Determinations. If 1 ml. of nitrogen is desired, set the arrow to the theoretical per cent nitrogen on the inner scale and read the sample weight indicated by the N (1 ml.) line on the outer scale. If 0.5 ml. of nitrogen is preferred, use the N (0.5 ml.) line.

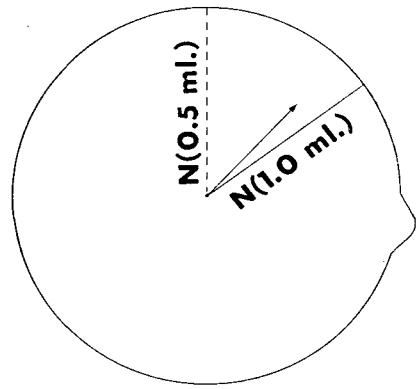


Figure 5. Nitrogen Slider

Scale up to same size as Figure 1

For Multiplying any two numbers (outer C and H scale and solid lines extending to indicator tabs are used). To multiply $M \times N$, set the solid line of the C indicator on M and the solid H indicator line on the index point of the scale. The indicator lines thus form an angle. Without disturbing the angle, move both sliders together so that the H indicator line falls on N. Read the answer under the C indicator line. The decimal point is set as usual in slide rule calculations.

For Dividing (use outer scale and solid C and H indicator lines). To divide M by N, set the C indicator line on M and the H indicator line on N. Move both sliders together until the H indicator line rests on the index position. The answer is indicated under the C indicator; fix the decimal point by an approximate calculation.

Multiple Operations. The slide rule can be used to perform operations of the type

$$\frac{M \times N \times O \times P}{Q \times R \times S}$$

by combining the multiplying and dividing steps described above.

Reciprocals. The reciprocal of any number may be conveniently obtained by using the Dumas nitrogen scales and the solid line of the indicator. To perform the operation $1/M$, set the indicator to M on the inner scale and read the answer under the same hairline on the outer scale. Fix the decimal point by an approximate calculation.

ACKNOWLEDGMENT

The authors wish to extend their appreciation to William L. Braun, Jr., and Alexander J. Tatun for assisting in the construction of the working models.

Grinders for Mulling Infrared Microsamples. Jesse S. Ard, Eastern Regional Research Laboratory, Philadelphia 18, Pa.

A VIBRATION grinder of exceptional simplicity was developed (*1*) for mulling a series of irreplaceable microsamples, and has proved satisfactory over several years of service. Mulling on a micro basis with this apparatus has been so convenient that the method has replaced all others for crystalline substances in the author's work, even when an abundant sample is available. Microsamples may also be ground with a reversed drill.

Mulls may be prepared with a mortar and pestle (*5*), by mashing between the cell windows (*3*), and by rotating cones (*6*); and methods developed for tissue mincing (*10*) are readily adaptable

to this purpose. Many substances are soft enough to be mulled on a cell window with a toothpick. Cotton, representative of particularly difficult substances, was reported to give a suitable mull preparation after grinding in a vibratory ball mill, and this was regarded as more effective in this special case than the use of ultrasonic energy or a Waring Blendor (*4*). As an alternative to mulling, one may use films deposited by vacuum sublimation (*2*) or from solvents selected for favorable depositing characteristics (*6*). Samples admixed with potassium bromide (*8*, *9*) or polyethylene (*7*) may be compressed into appropriate sections.

VIBRATION APPARATUS AND METHOD

The apparatus, Figure 1, consists of a commercial holder to vibrate small tools, and a specially constructed hammer and anvil.

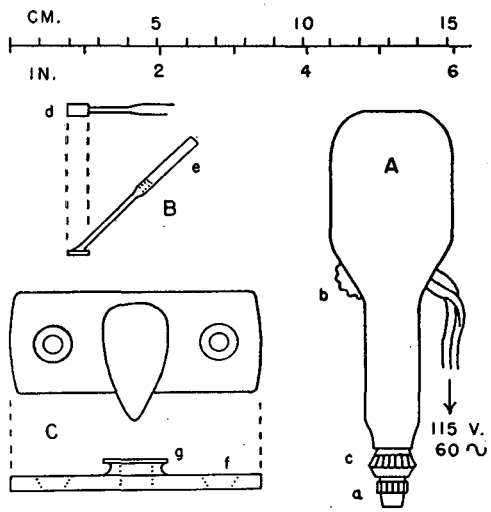


Figure 1. Apparatus for Mulling Microsamples

A. Holder for vibrating tools. *a*, chuck; *b*, on-and-off switch; *c*, one type of amplitude adjustment
B. Hammer. *d*, rectangular head; *e*, shaft to fit into chuck, *a*, of holder
C. Anvil. *g*, grinding plate, brazed to base *f*

In selecting a tool holder, important considerations are a chuck, a convenient on-and-off switch, and an adjustment for selecting the proper amplitude of vibrations. Lightweight holders, weighing about 0.5 pound and intended chiefly for light marking purposes, are suitable for mulling the microquantities discussed here. These should be distinguished from heavier holders (exceeding a pound), which are awkward with the small hammer described, and are more appropriate with a hammer five or ten times as large. Satisfactory types of holders for vibrating tools are available from laboratory supply, hardware, and handicraft stores. These usually are powered by 50- to 60-cycle, 115-volt, alternating current, and function by the simple action of an alternating magnetic field. [Known sources of the lightweight holders are: Ideal Industries, Inc., 1006 Park Ave., Sycamore, Ill. (Ideal electric marker); and the Burgess Battery Co., 180 North Wabash Ave., Chicago, Ill. (Vibro-Graver).]

The anvil has a top of polished stainless steel. This is flat with edges converging to a rounded point, so that the finished preparations can readily be scraped to a heap on the projecting point for the transfer. This plate is mounted on a pipe bracket, which makes a rigid base heavy enough to resist the vibrations. The metal junctions both here and on the hammer are brazed with silver solder.

The hammer head is a small flat piece with rectangular edges adapted for scraping, and brazed to it at an angle of about 45° is a shaft that fits into the chuck of the vibrating holder. The bottom portion is stainless steel, and the upper shaft is a section of brass welding rod.

The grinder is made ready for use by inserting the shaft in the chuck and adjusting the vibrations so as to give adequate grinding without spattering. After a trial, the ear readily recognizes the intensity of the hum associated with a favorable amplitude. With the usual mulling oils, this amplitude could vary over a wide range, but it may need restricting to a low level with special media of low viscosity.

In use, a drop of mulling oil is put near the center of the anvil, and the microsample is shaken into the oil. It is important that the sample be wet by the medium; otherwise the particles would be scattered by the vibrations. The vibrating hammer is passed over the mixture repeatedly. Beneath the head, the action during each stroke is hammering, shearing, sucking, and expelling; and from 30 seconds to 2 minutes are usually sufficient to mull the mixture into a translucent and creamy consistency. Prolonged or excessively violent action may darken the preparation by emulsifying some steel, but probably metals in this state would give only a generalized absorption without specific band structure. When completed, the mull is transferred to the cell windows by scraping and dabbing motions, with the power off when touching the windows. During this step, the flat scraping edges of the hammer are utilized to concentrate the sample into a heap near the point of the anvil. To clean, the grinding surfaces are wiped with absorbent paper and rinsed with acetone, and residues on the hammer are readily loosened by rinsing with the power on.

METHOD USING REVERSED DRILL

As the vibration grinder was satisfactory, it was not necessary to develop alternatives fully. Therefore, the following method had not had extensive usage, but in tests it seemed satisfactory.

A hole is drilled partly through a metal block, and the sample and oil are mulled together in this hole by the same drill rotating in the direction opposite to its cutting direction. At a properly chosen speed, the spiral slots of the drill continuously force the sample downward to the bottom of the hole, where it is concentrated, and mulling proceeds simultaneously as centrifugal force moves the mixture in a cycle against the shearing interfaces. If the drill is reversed again, and then gently and slowly revolved by the fingers in its cutting direction as it is withdrawn, the finished mull may be recovered as two neatly concentrated heaps just within the slots near the drill tip. Some laboratory stirrers have been adapted from kitchen mixers of the intermeshing twin-blade type, and many of these have a separate socket for turning a chuck in the counterclockwise direction as required for this purpose.

DISCUSSION

The outstanding previous method for mulling microquantities consisted in grinding the sample with oil directly between the cell windows (*3*). When this is accomplished skillfully, the economy of sample and the spectral results have unquestionably been satisfactory. It is rather difficult, however, to control the spreading, thickness, and pattern of distribution consistently while grinding the sample sufficiently, and the variable results have sometimes made it expedient to tolerate poor preparations and a low quality of spectra. Unless the sample is ground previously, this method would not be applicable to hard samples, but fortunately most organic chemicals are sufficiently soft. Even with soft samples, however, the windows are scratched by contacts between themselves and may need frequent resurfacing. The vibratory method has the uniform and intensive action characteristic of mechanical methods, and is thought to be far more versatile, convenient, and dependable. It decreases the waste caused by excessive spreading and unsatisfactory spectra, and it grinds harder substances. An outstanding difficulty in micromulling has been regathering the sample for continuing the action and for transferring, but with the vibration technique the grinding is done on flat surfaces, where simple scraping actions are effective for concentrating the sample.

The hammer described is of sufficient size to grind 2- to 25-mg. samples incorporated in a single drop of oil. Usually a drop of oil weighing from 12 to 25 mg. is shaken from a delivery tip 2 mm. in outside diameter, and the sample is then visually proportioned to this to give a creamy consistency when mulled. If the ingredients for the mull need weighing, the anvil plate can be made detachable and tared to make this easier. Larger samples can be handled, but they would spread and require an inconvenient number of grinding passes. On the other hand, smaller samples

are readily ground; and the method can be adapted to very small quantities such as those appropriate for manipulations under low-power microscopes. This possibility is of interest in criminology and for electron and x-ray diffraction work.

For infrared mulls, the sample is ground in an appropriate oil that does not need removal, but if an oil-free sample is desired, the oil may be flooded off with a volatile selective solvent like hexane. Preliminary results suggest that this procedure may be useful in the preparation of samples for the potassium bromide wafer method (*8, 9*); however, the usual advantages from grinding in an oil medium seemed to be decreaed with substances like potassium bromide and sodium chloride that fracture into cubes, probably because the surface of the cubical crystals is relatively low.

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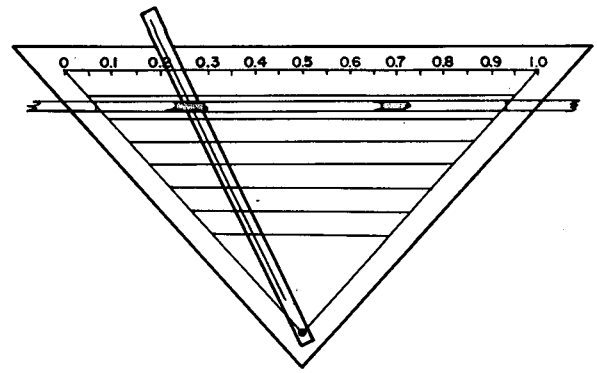
PRESENTED in part before the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 5 to 7, 1951. Mention of names is intended for convenience and must not be construed as an endorsement or recommendation by the United States Department of Agriculture over others not mentioned.

Device for Rapid Measurement of Chromatographic R_b Values. Anthony J. Glazko and Wesley A. Dill, Research Laboratories, Parke, Davis and Co., Detroit, Mich.

A PROPORTIONAL divider for measuring chromatographic R_b values, which has been used in this laboratory for more than 3 years, appears to offer certain advantages over similar devices recently described in the literature [Rockland, L. B., and Dunn, M. S., *Science*, **111**, 332–3 (1950); Nettleton, R. M., and Mefferd, R. B., ANAL. CHEM., **24**, 1687 (1952)]. As the scale is longer than the paper strip itself, the accuracy of measurement is as good as that obtained by manual measurements with a ruler, and the R_f values are read off directly from the end of the pointer. No difficulty is experienced with proper orientation of the paper strip, since the device is transparent and can be laid down directly over the paper strip, holding it firmly in place. This device was first described by the authors at a Symposium on Chromatography conducted by the Division of Medicinal Chemistry of the AMERICAN CHEMICAL SOCIETY in Chicago, September 1950.

The device shown consists of a transparent triangular sheet of plastic material, such as $^1/_{16}$-inch Lucite or Plexiglas. An R_f scale is inscribed on the hypotenuse, and a series of lines parallel to the scale is inscribed about 1 inch apart on the rest of the triangle. One end of a movable arm having an index line drawn down the middle is attached to the angle opposite the R_b scale with a metal pivot. All lines can be inscribed with a sharp knife or razor blade, and filled with India ink, colored crayon, or enamel to render them easily visible. Approximate dimensions are 18 × 18 × 24 inches. The movable arm is 0.5 × 18 inches.

In use the scale is placed over the paper strip and oriented so that the paper strip is parallel to the scale, with the starting point of the chromatogram on the left-hand leg of the triangle and



the limit of solvent travel on the right-hand leg. The movable arm is then shifted to intersect the spot on the paper strip whose location is being measured, and the R_b value is read directly from the scale. This proportional divider is based on the principal of similar triangles, and has proved to be the most rapid and practical means of R_b measurement used to date.

Simple Method for Differentiating between Borosilicate and Soft Glass. M. K. Carron and R. E. Stevens, U. S. Geological Survey, Washington, D. C.

THE use of solutions of index of refraction 1.472 as a means of separating borosilicate glass, such as Pyrex No. 7740, from soft glassware [*Chem. Eng. News*, **31**, 160 (1953)] prompts this report of an equally simple and rapid method, which has been used for several years in the laboratories of the U. S. Geological Survey.

The end of the glass, usually tubing or rods, is abraded in a small drop of water on a streak plate (or other unglazed porcelain surface) that is impregnated with phenolphthalein indicator. Soft glass almost immediately produces red streaks on the plate and colors the solution, whereas borosilicate glass causes no change. The mechanism of the reaction is the release of alkali ions into solution, aided by localized heating at the point of abrasion. The pH of the solution or suspension formed with soft glass is above 8.4; the pH obtained with borosilicate glass, which contains much less alkali, is too low to produce the color change. Although a fresh surface on the streak plate is necessary for each test, the area consumed is very small. Both sides of a 2.25 × 3.75 inch streak plate provide enough surface for a minimum of 50 tests. The streak plate can be easily cleaned and reimpregnated with phenolphthalein indicator; a single plate can be used indefinitely.

Two alternative methods for applying the same reaction are as follows:

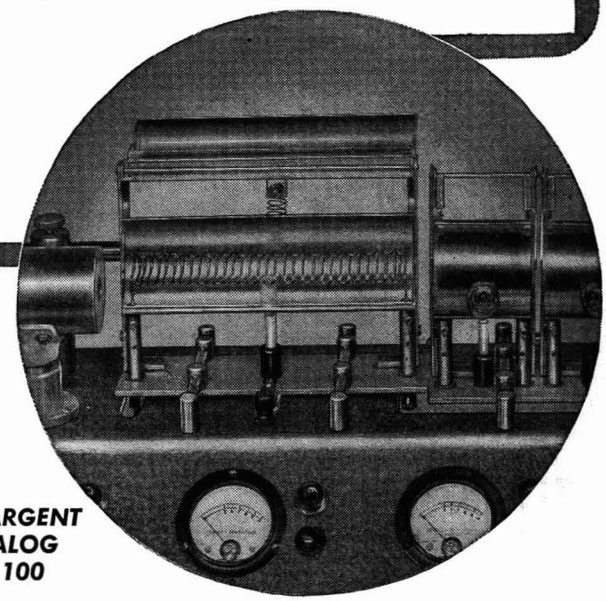
Abrade the glass in a small drop of water on a clean streak plate for a few seconds and apply a small dry piece of filter paper impregnated with phenolphthalein indicator. Soft glass colors the paper red; borosilicate glass produces no change.

Abrade the glass in a small drop of the alcoholic solution of phenolphthalein indicator and a drop of water on the streak plate. A red color in the solution indicates soft glass; no change indicates borosilicate glass.

The test is also useful in differentiating minerals using indicators of differing pH range, and is of interest in geochemical studies in indicating the pH that results from the solution of various silicate minerals in nature. Dolomite, $CaMgCO_3$, which turns phenolphthalein red, can be differentiated readily from calcite, $CaCO_3$, which does not. Talc, $Mg_3Si_4(OH)_2$, can likewise be differentiated from pyrophyllite, $4[Al_2Si_4O_{10}(OH)_2]$, with phenol red, the former giving a red color, the latter yellow [Stevens, R. E., and Carron, M. K., *Am. Mineralogist*, **33**, 31–49 (1948).]

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S-21570 COMBUSTION APPARATUS—Automatic, Micro and Semi-Micro, Radiant Furnaces, Static Triple-Section Burning Furnaces, Directional Sequence Program, Sargent, (Pat. Pend.). This apparatus is suitable for all micro and semi-micro combustion procedures and is extremely flexible in use with regard to both the type of sample to be analyzed and the technique employed in the analysis. It allows the establishment of optimum conditions to suit any type of sample, including both highly volatile, rapid burning compounds and very refractory materials.

The unit employs two furnaces, one being seven inches in length and for heating the tube filling, and a second for burning the sample. The latter is of triple section construction, utilizing three two and one-half inch small furnaces on a common base, with separate shells and heating elements. The long furnace and the three sections of the burning furnace have individual autotransformer controls for temperature adjustment, power switches, fuses and pilot lights. Individual thermocouples and direct reading pyrometers are also provided. All furnaces are of the hinged Sargent radiant heating type with open sided elements. Both furnace units may be pushed back to expose the combustion tube for rapid cooling.

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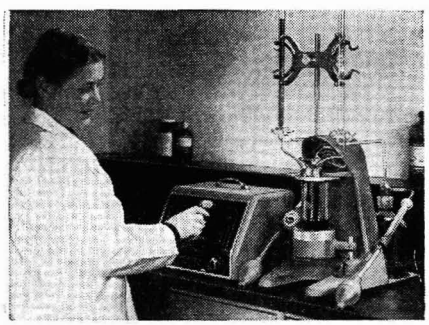
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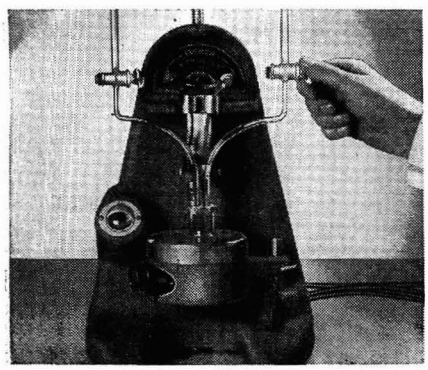
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INSTRUMENTATION



National Bureau of Standards program on basic instrumentation is urgent and important, as our supply of fundamental information is running very short

by Ralph H. Müller

IT WOULD be inappropriate and, certainly, untimely for us to discuss the late furor over the Astin dismissal and reinstatement. This tragicomedy of inspired errors and belated rectification interests us only in terms of the resultant wreckage and how it affects progress in American instrumentation. The budget reduction for the National Bureau of Standards has alarmed instrument manufacturers; but, for the time being, they must accept a curtailment of services for which they have paid in the past, and are more than willing to pay in the future. The budget reduction no doubt reflects the Administration's general effort to decrease all national expenditures, but this unfortunate incident must have contributed to some degree to the reduction. It is too much to expect our legislators, and the general public which they represent, to share the scientist's unswerving and enthusiastic belief in the bureau and what it represents.

Even the scientist, preoccupied with his special interests, is likely to overlook the wide and diversified activities of NBS. Some years ago, in surveying the American instrument industry [IND. ENG. CHEM., ANAL. ED., **12,** 511 (1940)] we were required to learn the intimate details of the bureau's responsibilities and accomplishments. Our initial pride and satisfaction with its fame proved to be wholly inadequate. We are all prone to think of its services in terms of our personal requirements—for standard samples, calibration of weights, standard cells, etc. Even despite personal acquaintances, we are likely to forget its distinguished "faculty" of past and present scientists such as Lundell, Diamond, Priest, Hoffman, Bright, Crittenden, Wichers, Meggers, Brickwedde—selected at random from a list which could fill this column.

One of the 15 or more divisions and sections, there is not one which is not concerned with some aspect of instrumentation or the search for new and improved methods of measurement. In some divisions, this is the principal objective.

Program of Basic Instrumentation

Four years ago, E. U. Condon, former director of the bureau, asked, "Is There a Science of Instrumentation?" [*Science,* **110,** No. 2858, 339 (1949)]. This is a question which we could have answered in the affirmative 15 years earlier, but it is always useful to have someone of importance raise a provocative question. He was urged at about that time to implement his opinions by establishing the Office of Basic Instrumentation under the able direction of W. S. Wildhack. The official statement of its purpose was:

> The basic instrumentation program at the National Bureau of Standards is cooperatively sponsored by the Office of Naval Research, Office of Air Research, and Atomic Energy Commission, and is an extension and continuation of a limited program in 1948, sponsored by the Office of Naval Research. The scope of this program includes:
>
> I. Experimental and theoretical projects in theory, development, and evaluation of instruments.
> II. Reference and consultation on instrument problems and development, arising not only in the laboratories of the sponsoring agencies and NBS, but in other governmental, industrial, and educational laboratories as well.
> III. Critical surveys of performance of instruments in selected fields.

This is a program of urgency and importance and one which cannot be sold to our universities or industry. We know this—we tried! A few of the problems which were proposed included studies on design of corrugated diaphragms, electron interferometry, hypsometry, strain and displacement, improved microscopes, photomultiplier design, mutual inductance transducers, and spring transducers. To a large degree, problems were chosen which could be done only at NBS. In ordinary circumstances, whether it be in the university, industry, or the armed forces, the search for a new instrumental principle is entirely secondary to some other aim: the completion of an urgent research problem, the more rapid manufacture of a product at lower cost, or the development of an improved weapon. Indeed, if such research is sponsored, there is almost a moral obligation to stop instrumental developments as soon as something acceptable has been found. There is no particular point in bemoaning this situation because it is a small part of our national headache—the need for more pure, "useless" research. Far too much of what passes for pure research has a string attached to it. The string has a finite length and often turns out to be a rope.

Since its inception, the Office of Basic Instrumentation has issued quarterly progress reports. Despite the competence, ingenuity, and outstanding ability of the staff, and the fundamental importance of the problems, the most frequent remark is "no progress because of a lack of personnel."

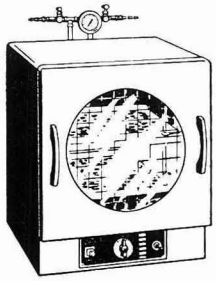
It will be astonishing, indeed, if these good people are not still more hampered in the near future. It is more than likely that in restricting its general activities, the bureau will have to place the major sacrifice on long-term research and concentrate on its more routine functions.

An American scientist instinctively associates the National Bureau of Standards with related establishments such as the National Physical Laboratory in Teddington, the Reichsanstalt, or the Bureau Internationale des Poids et Mesures. We have been indissoluble partners with these famous institutions in maintaining international standards.

These renowned laboratories, like our own, have contributed immeasurably to the science of precise measurement. Their reputation and prestige were jealously guarded but well assured by a constant roster of able and distinguished staff. Long before we became addicted to alphabetical confusion in our national life, such certification as NBS, NPL, or PTR was readily understood by scientists throughout the world.

WILL **Laboratory Equipment**

NEWS OF THE MONTH

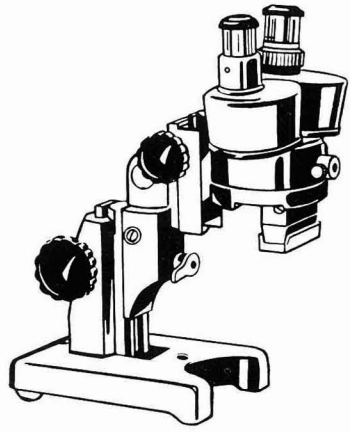


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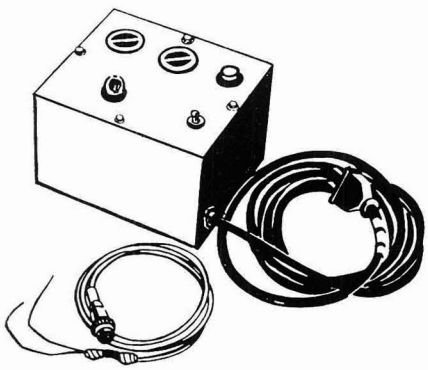
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INSTRUMENTATION

The scientists needs little encouragement or goading to convince him that work of such importance should receive handsome support. Actually, it is difficult for him to understand the attitude of his nontechnical fellow citizen. The latter is apt to regard NBS as authoritative in the legal or governmental sense and this is just enough to put him on edge and become constantly suspicious of any possible infringements of his personal privileges.

The bureau people would be the last in the world to assert that they are the sole custodians of exact knowledge or method. It is precisely because they strive to combine the best of all known techniques that they succeed in earning universal approval and acceptance. More important yet is their constant effort to improve and refine techniques. These are things for which they are uniquely fitted and for which others have not the patience, experience, or dedication.

The foreign equivalents of NBS have had minor upheavals, but one would infer that they were trivial because their distinguished record could not be possible in an environment which was not consistently favorable. It would be most interesting to compare their budgets with that of NBS on the basis of their respective national economies.

The American apparatus and instrument industry owes its origin very largely to the Scientific Apparatus Makers of America. In the post World War I period, their untiring efforts helped establish the infant industry. This organization was instrumental in establishing the *Review of Scientific Instruments* and largely maintained it until it was absorbed by the American Institute of Physics. This is a matter of historical significance and solid accomplishment.

But we wish to ask most respectfully, "What happened?" For several years, it has issued innocuous and obvious statements about our instrument industry. Occasionally, the old fire breaks out and its officers dash out of the comfortable seclusion of Greenbrier to gnash their teeth at the "impudent foreigners" who also make good instruments and try to sell them to us. We are all the more curious and bewildered because the members are all instrument manufacturers. Many of them are so efficient, progressive, and so far ahead of the times that their foreign worries are solely matters of export—not import. It would seem that an organization with such a record of fine accomplishment could promote dynamic and progressive ventures to ensure the

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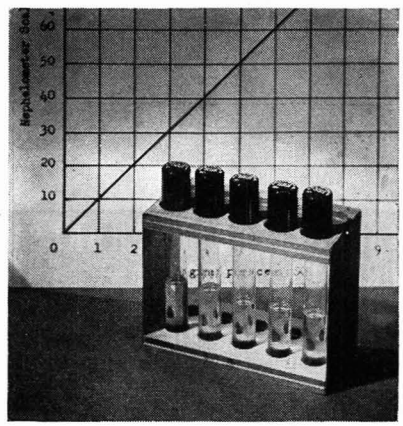
The Nephelometer is useful in determination of butter fat content in dairy products, and has similarly been helpful in assay of cholesterol in blood chemistry.

PRECISE NOTATION FOR HAZE

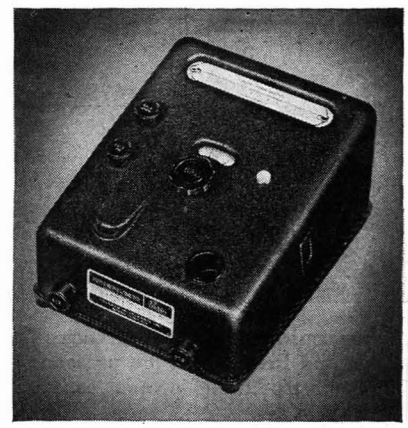
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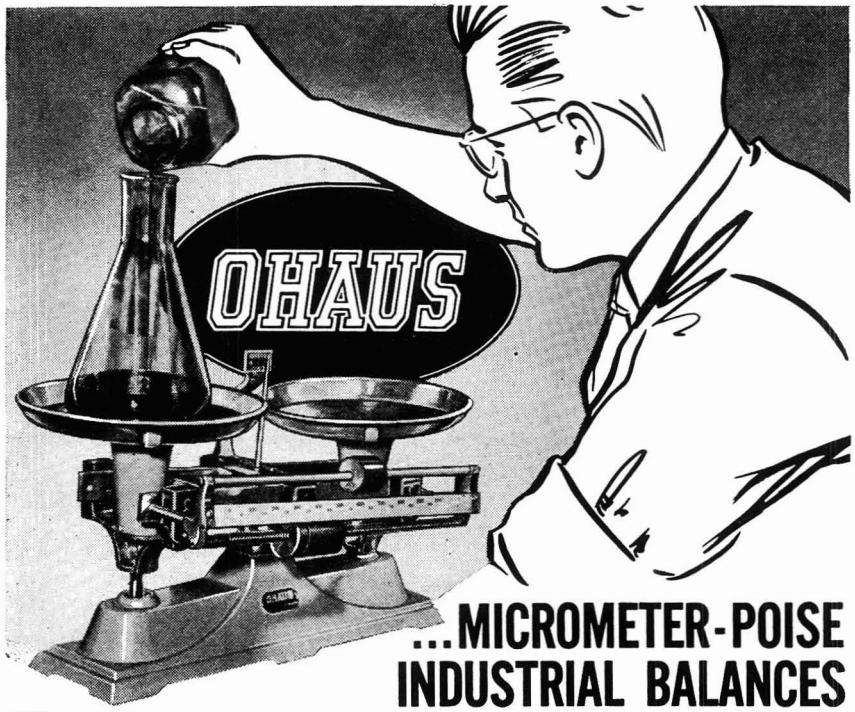
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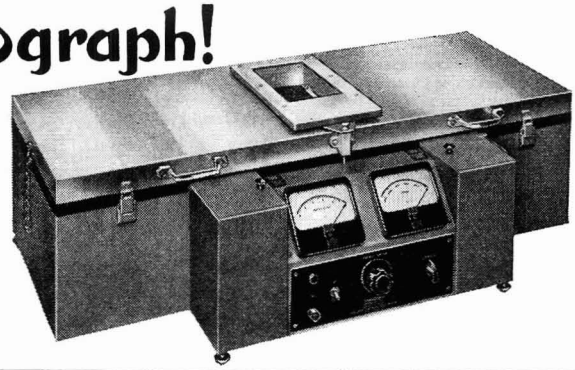
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INSTRUMENTATION

progress of instrumentation in all of its aspects. It was once maintained, in high places, that America had attained industrial and technological maturity and that the larger problem confronting its people was the more equitable distribution of its benefits. It took a long time to dispel this nonsense despite its obviously humane intent. Instrumentation cannot be fostered or promoted by conserving our present resources or by loudly proclaiming our prerogatives.

Rapid Advances

It is difficult to keep up with the rapid advances in instrumentation. There are few occasions when the advance seems other than prodigious, but when one considers the enormous amount of scientific and technical work which is being done and published, the development is not extraordinary. It becomes all the more apparent, as in other fields, that we are running short on fundamental information. For this reason, it is most urgent that the Office of Basic Instrumentation be supported to an extent commensurate with its importance. If such support has to come almost exclusively from the armed services, its proper function will not be served. It will, perforce, develop gadgets and necessary adjuncts to "Buck Rogers" warfare and the more fundamental needs will be neglected. In being realistic, one cannot ignore the urgency of military necessity, and as long as persistent, scratching noises emanate from the international woodwork, we shall have to live with these things.

The reduction of the National Bureau of Standards budget is expressible in some definite percentage, the exact value of which we do not recall at the moment. We believe that its budget should be increased tenfold, fully aware that any number of people can prove that the suggestion is extravagant and absurd, with Q.E.D. attached. We merely ask that the critic examine all other governmental expenditures for science and technology and compare them not only in sum, but against the demonstrated prestige, experience, and ability of the bureau's personnel.

There have been much elation and shouting from the housetops at the final decline of the Ivory Tower. At each celebration, another promising scientist has been kicked upstairs to become an executive. Research direction has become a higher-echelon decision and the hunch becomes a project. It works, and the royalties roll in. Some day we shall be caught with inventory troubles and we may call for bigger and better Ivory Towers. It's later than we think.

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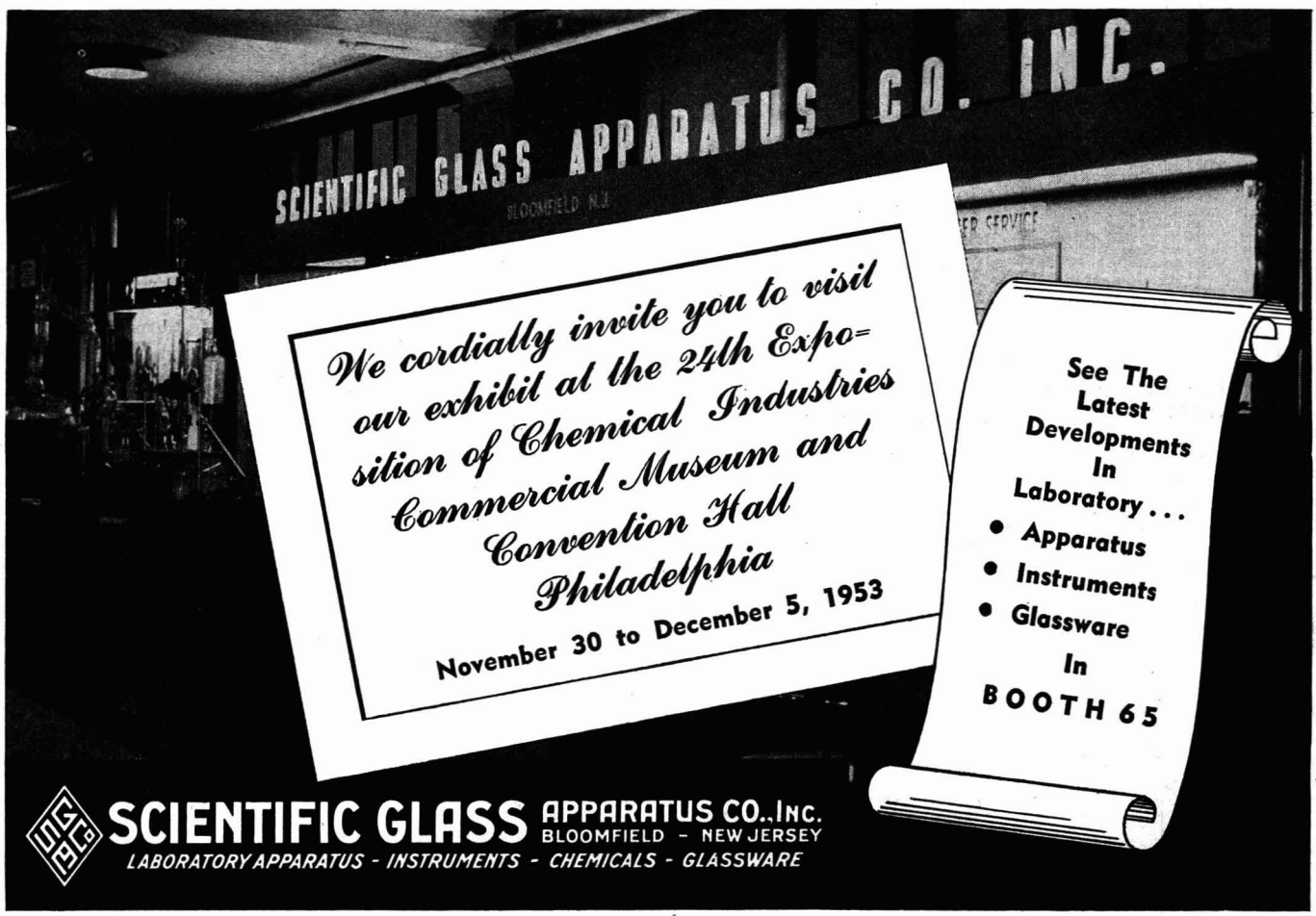


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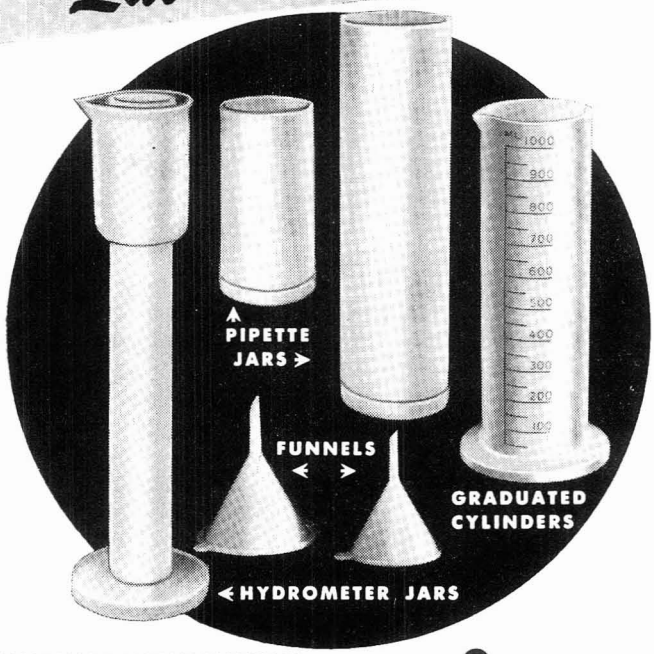
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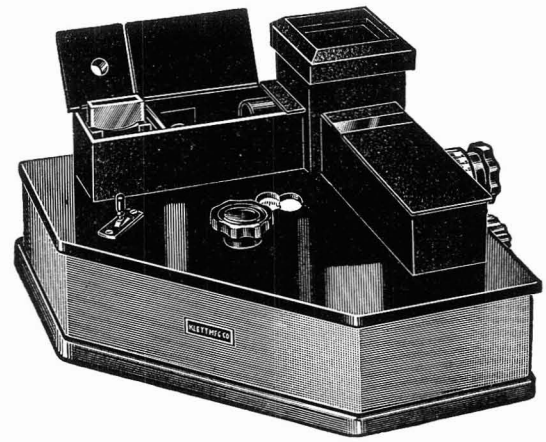
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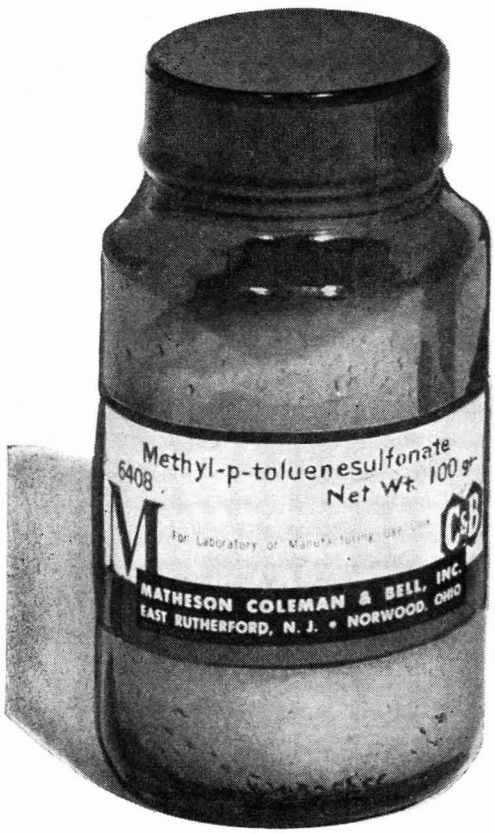
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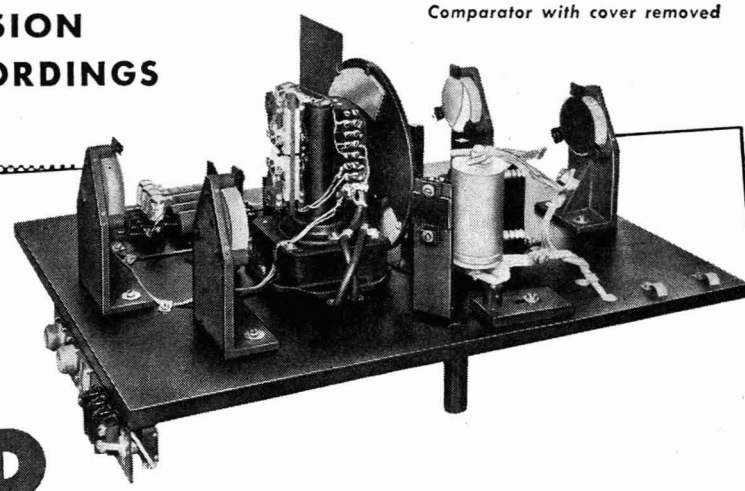
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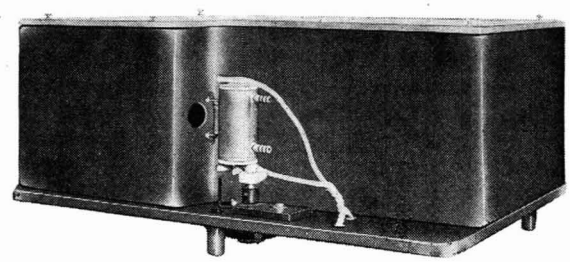
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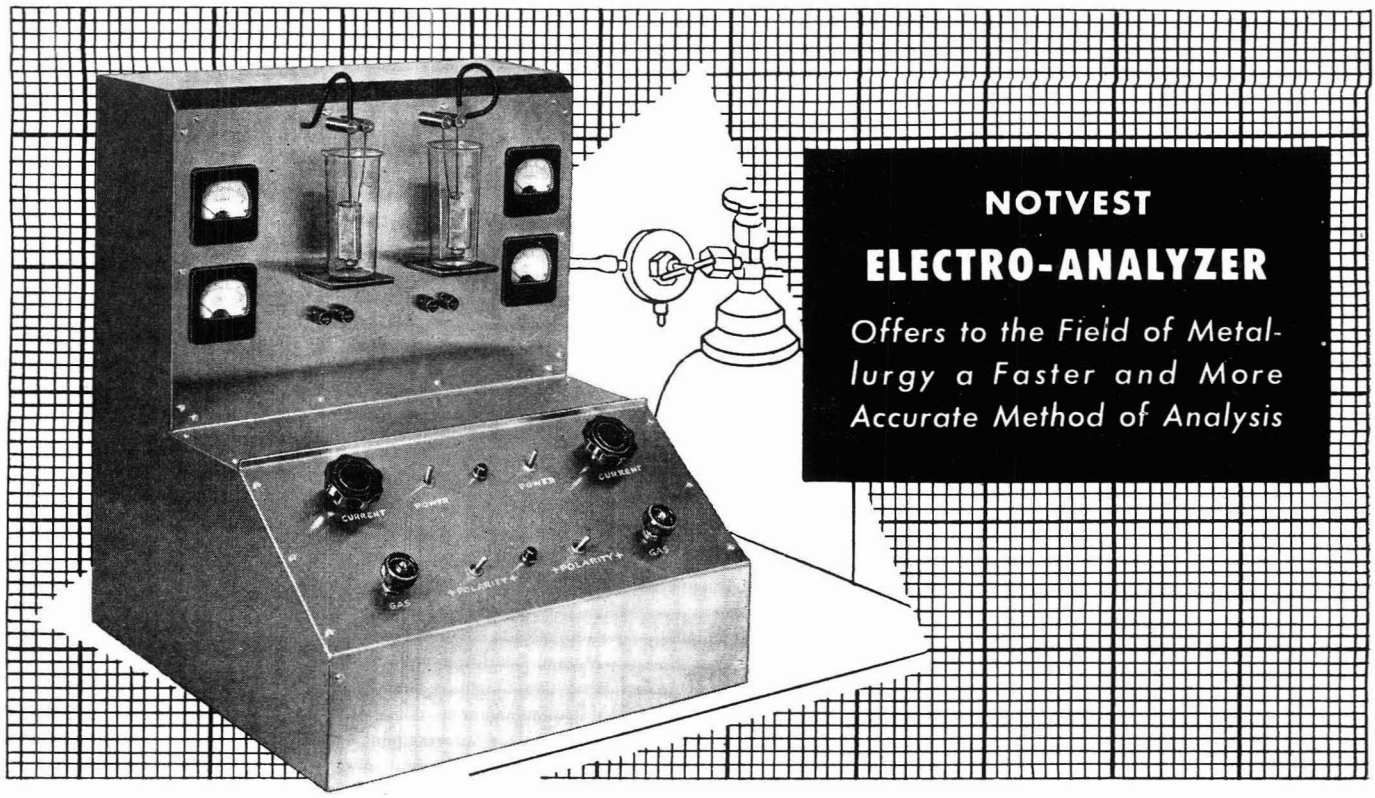
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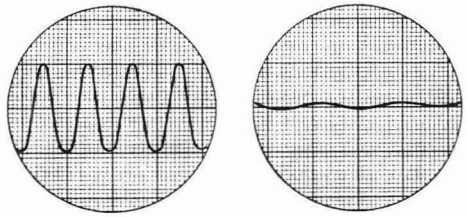
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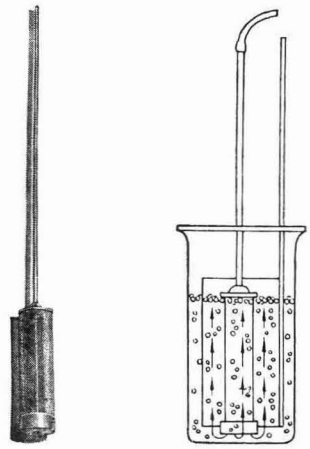


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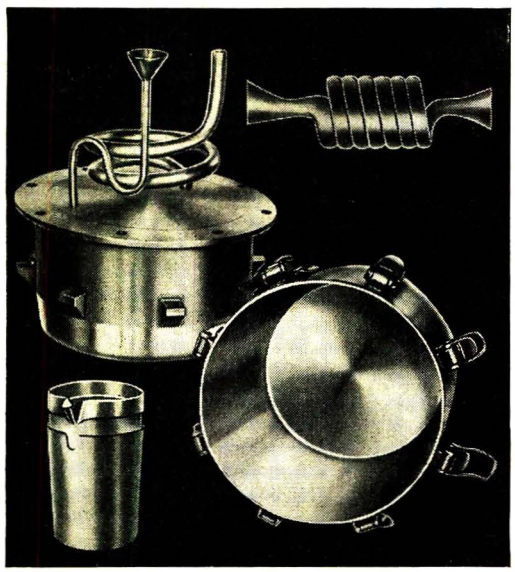
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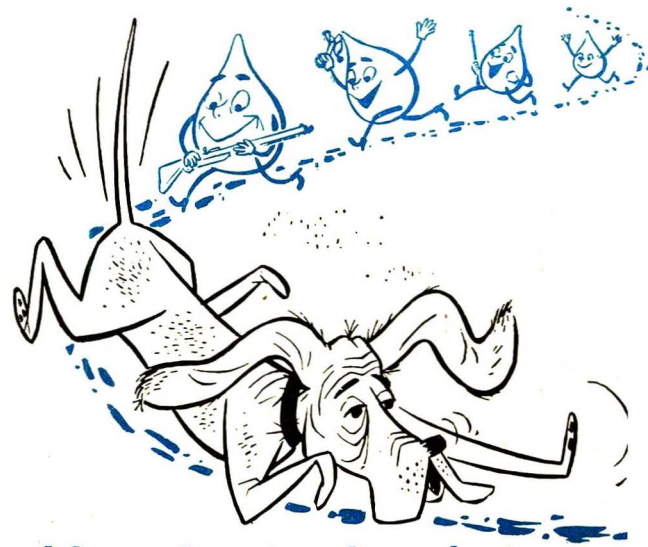
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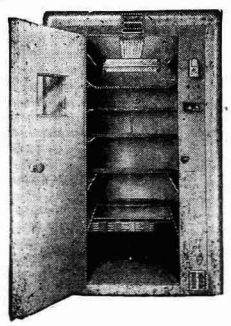
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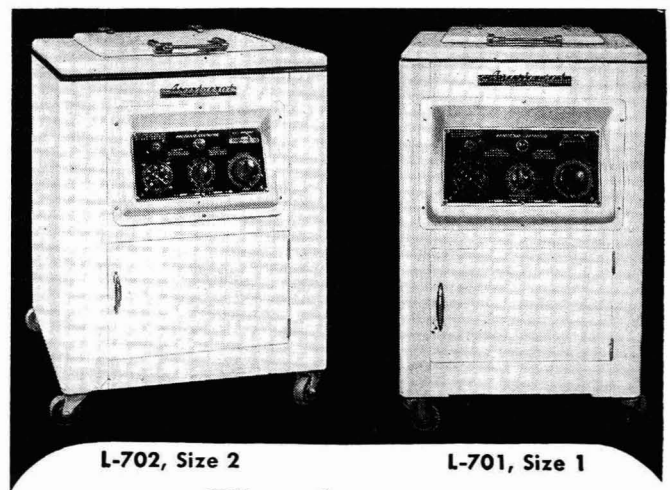


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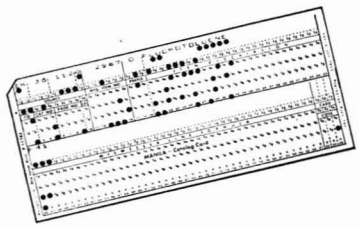
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4 OUT OF MORE THAN 3500

Fine needles, fine haystack...

Why is *o-Benzoic Sulfimide* (Eastman 38) like *2-Aminobenzothiazole* (Eastman 3940)?

One of our senior chemists, who knows the Eastman catalog about as well as he knows his children's names and ages, got to brooding recently that given one of these compounds, even *he* wouldn't have been able to name the other right off as one of its nearest relatives in our list. (Both consist of a C_3NS heterocycle fused to a carbocycle.) His unease about the difficulty in picking up such relationships among his own merchandise

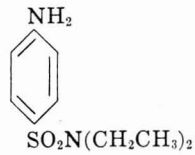


pricked him to spend a good many hours at home making up a deck of cards coded for each compound, that could be shuffled in various ways.

We now learn that another chemist, who works not for us but for Remington Rand, has done the job by punched cards. We ourselves have encoded a fair amount of chemical data on punched cards, but this fellow has done it by the new Wiswesser notation for every Eastman Organic Chemical having a known structure. Thus electromechanical brains, such as are ensconced in many large organizations, can fill in their idle moments by discovering all sorts of important relationships among the more than 3500 organic compounds available from a single, completely dependable source—namely, us.

If you want to know more about what this man has done, or if you want to purchase our catalog in punched card form, write Remington Rand Inc., 315 Fourth Avenue, New York 10, N. Y. In its conventional book form, the catalog remains free of charge. If you need a copy, write us.

Sulfa for thyroxine...



There's a curious relationship—of no physiological significance, we're sure —that links the sulfa drugs with thyroxine: several of the former, diazotized, make good colorimetric reagents for the latter. This was discovered in 1947 by some folks in Melbourne, Australia, who felt the need of an alternative chemical assay for the tetraiodo amino acid that is the active principle of the thyroid gland. They tried a large number of amines, looking for one which could be easily diazotized, produced a strongly colored product when reacted with thyroxine, and was readily soluble in n-butanol. From the favorable behavior of the sulfa drugs in the trials, they took a lead and finally fixed on *N^1,N^1-Diethylsulfanilamide*. They wrote a good, comprehensive paper on this work and published it in *The Biochemical Journal*, (*42*, 475(1948)). There, for all *we* knew of it, it languished until a call came the other day from the Montreal office of one of our distributors.

We have a large number of such distributors scattered from Atlanta to Zurich. They are very helpful to people who prefer, at no extra cost, to do their business with a human face rather than with a squiggle at the bottom of a letter or a squawk from a telephone. In this case the man in Montreal had a friend who wanted to know if we could make some *N^1,N^1-Diethylsulfanilamide*. We could. Thus were born Eastman 6900 and an abstract of how to use it in the assay of thyroxine. The former costs a dollar a gram and the latter is free.

Other people's business...

Without previous experience in the manufacture of m-cresoxyacetic acid, we accepted an order for several kilos of the compound the other day. This is not exceptional. The generalized nature of our synthetic operations often permits us to make chemicals in larger-than-laboratory quantities more efficiently than our customers can do it for themselves. Accustomed as we are in these cases to keep our nose out of other people's business, we didn't ask any questions. Nevertheless, we did note that a team from a university in South India had broken into print not long ago with the tidings that m-cresoxyacetic acid makes an excellent reagent for separating thorium from the rare earths of the local monazite sands and from uranium. Impressed, we called the compound *m-Toloxyacetic Acid* in accordance with *Chemical Abstracts* nomenclature and added it as Eastman 6883 to our list.

By writing to us, you can obtain any or all of the following: 1) a frank appraisal of our readiness to supply larger-than-laboratory quantities of any organic compound you require; 2) an abstract of the procedure for thorium; 3) 10 grams of *m-Toloxyacetic Acid* for $3.50 to carry it out with; 4) an explanation of the system by which we renamed it as we did.

In our List No. 38, you will find more than 3500 other Eastman Organic Chemicals. If you haven't a copy, write to *Distillation Products Industries*, Eastman Organic Chemicals Department, Rochester 3, N. Y.

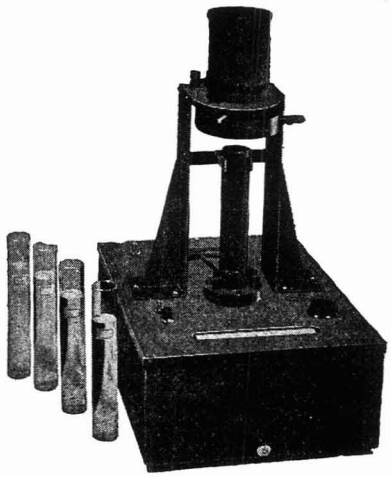
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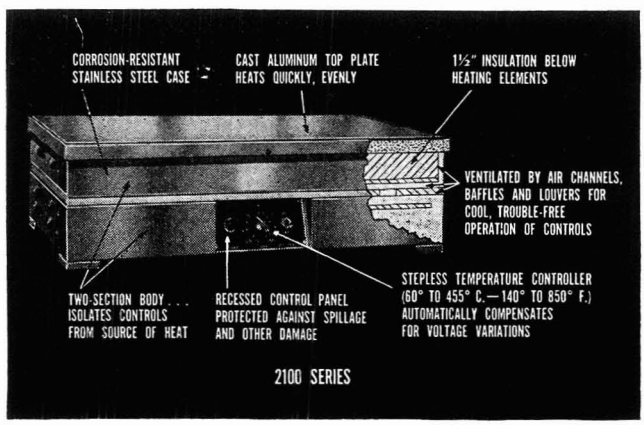


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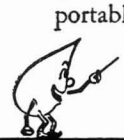


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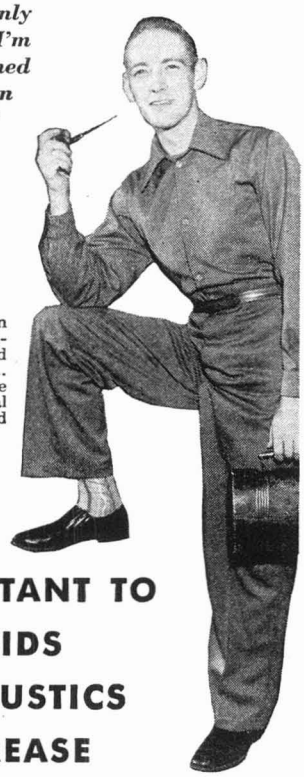
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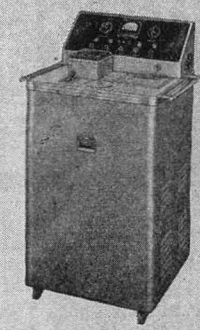
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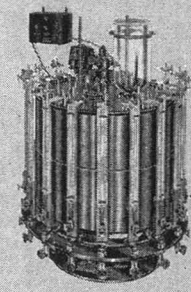
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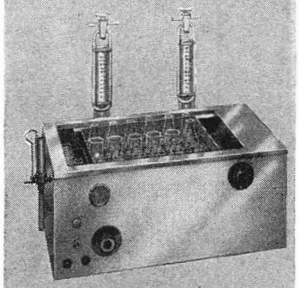
The many advantages of Aminco apparatus are described in BULLETIN B-2185.



WARBURG APPARATUS

DUBNOFF SHAKER-INCUBATOR

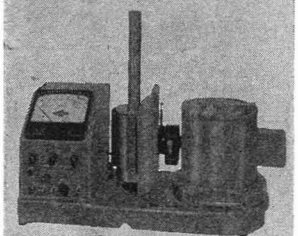
Up to 30 specimens can be shaken simultaneously in this improved apparatus at temperatures from 25° to 100° C., with a sensitivity of plus-minus 0.015° C. within the flasks. Intended for metabolic studies not requiring the measurement of gas exchange. Accommodates two types of racks for holding beakers or Erlenmeyer flasks. Shaking speed is constant regardless of line-voltage fluctuations. Has provisions for gassing. Flasks may be simultaneously cooled, gas equilibrated, incubated, or boiled. Many other features described in BULLETIN B-2239.



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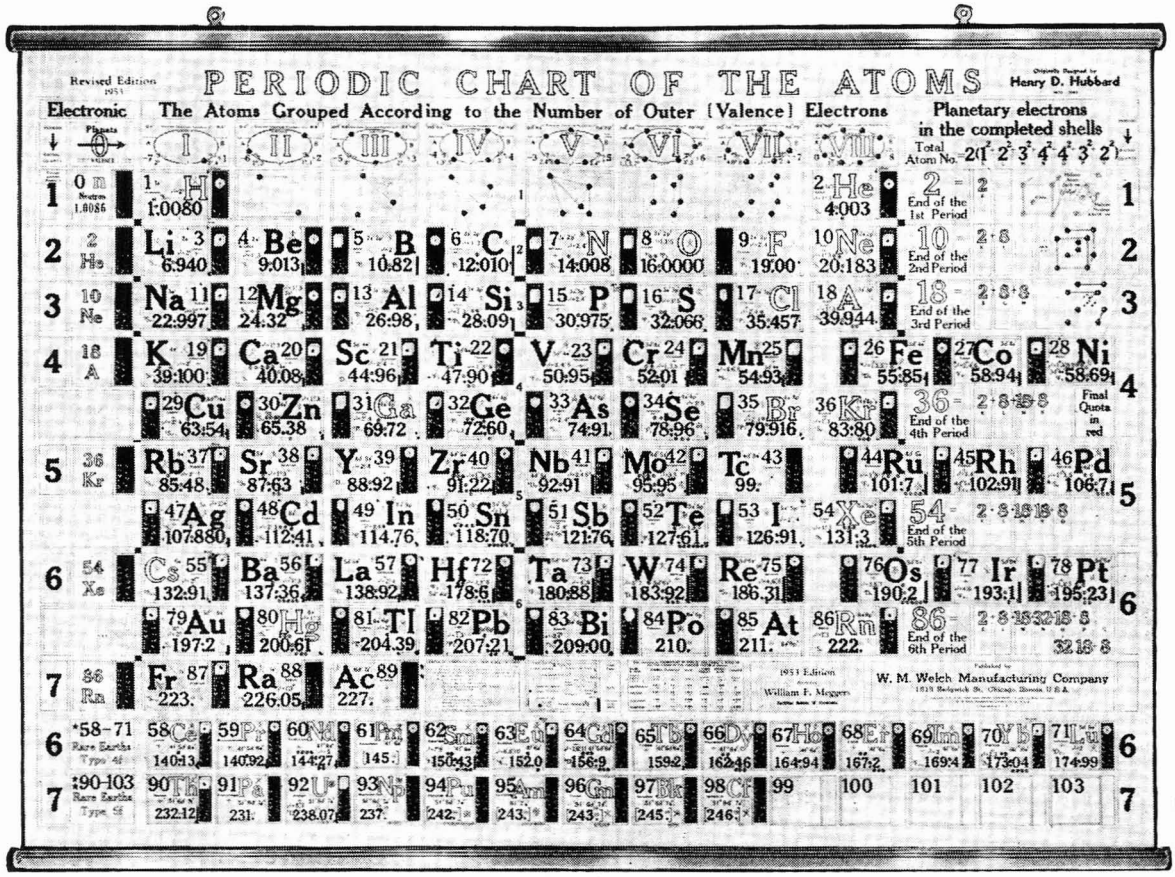
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X-Ray Diffraction Camera

A flat plate camera with a high degree of utility for x-ray diffraction work has been designed by North American Philips Co., Inc. The new unit is said to be useful for investigations which cannot be handled effectively with a powder camera or a diffractometer. It can be used for Laue work or with monochromatic or filtered radiation. Major application is expected to be the study of metals, but it is also useful for powdered materials, plastics, and, to some extent, semisolids and liquids.

The camera consists of 3 elements. A stationary specimen mount accommodates not only planar sections of metals, crystals, compacted powders, or plastics, but also wires, fibers, powder specimens mounted on fibers, or materials in capillary tubes. A combination collimator mount and motor-rotated back reflection cassette is pierced by a central hole for insertion of either a parallel beam or focusing type collimator. A forward reflection cassette has a motor drive for rotation and can also be utilized as a specimen support. Both cassettes use film of 4 × $3^1/_4$ inch size. **2**

Temperature Standards

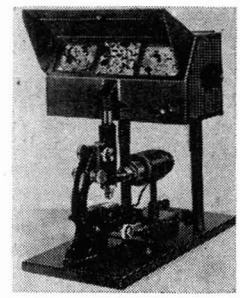
Weiller Instruments Corp. has introduced improved temperature standards consisting of various metals and metallic mixtures that are heated to their melting point in a graphite crucible with an electric heater wound directly on the graphite to minimize heat inertia. The crucible is bisected by a graphite partition that contains two cavities for insertion of the thermometer or thermocouple being calibrated. Both the standard metal and the thermometer or thermocouple are fully protected.

The sensing element of a controller can be inserted in one cavity and set at a temperature slightly above the melting point of the standard to make the operation semiautomatic.

Standard materials available include sodium, tin, lead, zinc, silver, and copper. They range in melting points from 97.8° to 1083.0° C. **3**

Grain Size Determination

An accurate means for determining grain size in copper and copper base alloys is provided by General Scientific Equipment Co.'s new Micrographex comparator. Identification of grain sizes from 0.010 to 0.200 mm., as classified by ASTM designation E-79, can be quickly accomplished, states the company.



Designed primarily for grain size determination, the comparator is flexible enough for many other particle size determination uses. It may be used with any standard microscope for either transmitted or reflected illumination. Magnification can be adjusted for specific applications. **4**

Standardization Equipment

An instrument standardization console has been developed at General Electric Co.'s general engineering laboratory for use in development, design,

Circle desired items for further information on items listed in this section

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NOVEMBER 1953

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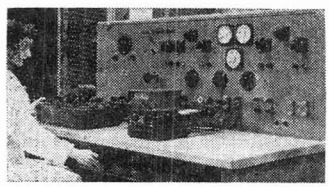
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and standardization or calibration of most electrical instruments. The equipment supplies low-distortion regulated power in the range of 50 to 3000 cycles per second. Current supplies and a.c. and d.c. voltages are provided on bus facilities up to 150 amperes, 750 volts.



The design extends the accuracy and stability of d.c. potentiometer standardization equipment into the audio-frequency range of alternating current instrument calibration, states GE.

The console is composed of a cabinet section which contains most of the subassemblies and a table section which serves primarily as a work area. A regulator is used to provide stable voltage to all components affecting the calibration. The d.c. potential supply is made up of a rectifier unit and filtering unit. **5**

Constant Temperature Room

Electric Hotpack Co., Inc., has a walk-in constant temperature room which can be varied in size from 2 to 8 feet. The unit is easy to assemble and install or to disassemble and relocate, claims the manufacturer.

The Hotpack constant temperature room provides a walk-in box that will hold temperature to within $^1/_2$° C. for long periods. It can be regulated for temperatures from 5° to 40° C. Construction is of metal, primarily aluminum.

At maximum size, the room is 8 feet long, 4 feet wide, and 7 feet high. The length can be reduced in 2-foot steps down to 2 feet, with width and height remaining constant. Other features of the unit include a door window for observation of the interior, adjustable shelves providing up to 120 square feet of storage space, a control which switches on lights when the door is opened, and devices which make it impossible to be locked within the room. **6**

Inductance Bridge

An incremental inductance bridge for measuring the inductance of iron-cored inductors when there is a d.c. component of current present is being marketed by Waters Mfg., Inc. The compact instrument is completely self-contained and requires no accessories.

Adjustment of only one balance control is necessary to operate the bridge. The range of values obtainable is 1 to 200 henries at ±3% accuracy. Current values of 1 to 500 milliamperes d.c. can be selected by the operator. **7**

Soil Nitrogen Determination

Equipment and a new method for the determination of available soil nitrogen have been introduced by Hellige, Inc. The test differs from tests for nitrates and ammonia in that it determines the amount of substances in the soil which can be readily converted to available nitrogen for use by crops.

Equipment used for the test include a colorimetric comparator, a color plate with 5 permanent precision glass color standards, as well as glassware and reagents. **8**

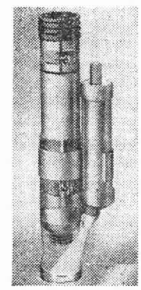
Electronic Counter

Atomic Instrument Co. has a new counter with a maximum capacity of 1,000,000 counts and a speed range of 0 to 5000 counts per second. All counting, indication, and transfer is done within cold-cathode glow transfer tubes. These tubes have bright red neon glows opposite circular spacings numbered from 0 to 9 to show the accumulated count.

Two units can be run in cascade, one feeding millions into the other. A jack in the rear of the chassis provides for remote control connection. The instrument will accept positive or negative pulses or sine waves of 4 to 60 volts. **9**

Brinnell Microscope-Reader

Pacific Transducer Corp. is offering a microscope-reader for accurate measurement of the diameters of indentations made by ball indentors of all Brinnell hardness testing machines. The microscope can also be used to test the accuracy of the testing machine itself.



The device features a reticle in a flat-field optical system and a self-enclosed concentrated beam of light provided by a prefocused battery illuminator. It offers a clear image of the indentation with the sharp image of the reticle superimposed. The Brinnell microscope-reader has a magnification of 20 diameters. Its scale is calibrated in millimeters and tenths of millimeters and has a total length of 7.0 mm. **10**

Radiochromatogram Scanner

An automatic system for exploring distributed radioactivity on paper radiochromatograms has been developed by Nuclear Instrument & Chemical Corp. The system locates and estimates quantitatively the components separated on a chromatogram by systematically scanning the paper strip with a thin-window Geiger counter.

The Actigraph system consists of a strip feeder, a lead shield which con-

(Continued on page 44 A)

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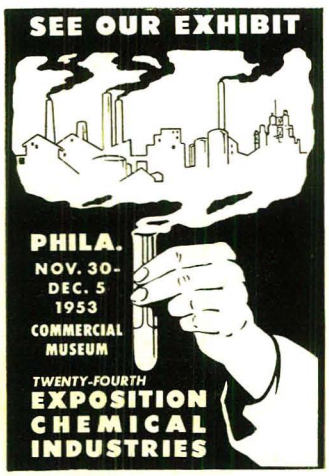
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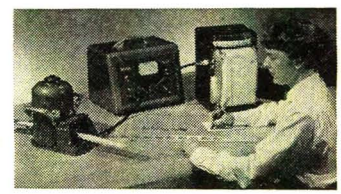
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NEW PRODUCTS, continued

tains the mica-end window counter and a collimating slit, an analytical count rate meter, and a chart recorder. The strip chromatogram is taped to a long metal strip table, then passed through the lead shield and the rollers of the strip feeder. The movement of the paper strip is synchronized with the movement of the recording chart so that a direct comparison can be made after the strip has been scanned.



The rate of progress of both the chart and the strip can be set to any one of eight different speeds from 0.75 to 360 inches per hour. Special tables permit the use of the instrument as a simple sample changer or, with absorbers, to produce a characteristic absorption curve. **11**

Acetonedicarboxylic Acid Esters

Large scale production of the diethyl ester of acetonedicarboxylic acid has been announced by Smith-New York Co., Inc. Other esters are available in laboratory quantities.

The esters are stable and enter into all reactions of the beta-keto ester type. Because the acid has 2 active, symmetrical methylene groups, it forms symmetrical ring compounds containing nitrogen or oxygen, and even benzene derivatives. It is used in the Robinson synthesis of atropine and similar alkaloids. It may also be used for the production of pyrazolones and piperidones or of insecticides of the allethrin type. The material forms a sodium derivative in alcohol and a sodium salt in water. **12**

Reagents

Five chemicals have been added to the certified reagents of high purity supplied by Fisher Scientific Co. in laboratory quantities.

Ammonium fluoride, a reagent for silicates, is available with a chloride content of 0.001% maximum and a heavy metals content of 0.0005% maximum.

Silver chloride is offered meeting the following specifications: copper, 0.001%; iron, 0.001%; heavy metals, 0.005%; nitrates, 0.001%.

Fisher's lump antimony certified reagent has low impurity limits to aid

For further information, see coupon on page 41 A

NEW PRODUCTS, continued

proper duplication in trace sensitive research.

Resorcinol of high purity is useful as a reagent for zinc and as an indicator for reducing substances in filter paper chromatography, as well as for organic synthesis.

Hydrogen peroxide is being produced by Fisher with a limit of 0.0005% sulfate for yielding low blanks in acid digestions of organic materials. The reagent has a maximum heavy metals content of 0.0001%. **13**

Hot Plate

A 7-inch diameter round hot plate is being sold by Thermo Electric Mfg. Co. Its thermostat provides stepless control from room temperature to 270° C. The surface plate temperature is claimed to vary less than 3° C. at any point over the full heating range. The polished cast aluminum plate reaches top temperature in 25 minutes.

Sockets welded to the unit accommodate a clamp and rod for support of apparatus above the plate or for support of the plate itself. It operates on 110-volt, 25- to 60-cycle a.c. power and has a rating of 660 watts, 6 amperes. **14**

Conductivity Bridge

Industrial Instruments, Inc., has developed an improved general purpose conductivity bridge for electrolytic conductivity and electrical test measurements.

The Type RC-16B bridge has variable sensitivity control up to a maximum of 0.33%. Sensitivity is regulated by a knob on the front panel. Range of the instrument is from 0.2 to 2,500,000 ohms with an accuracy of 1% of measured resistance. Two bridge source frequencies are available—at line frequency and 1000 cycles per second.

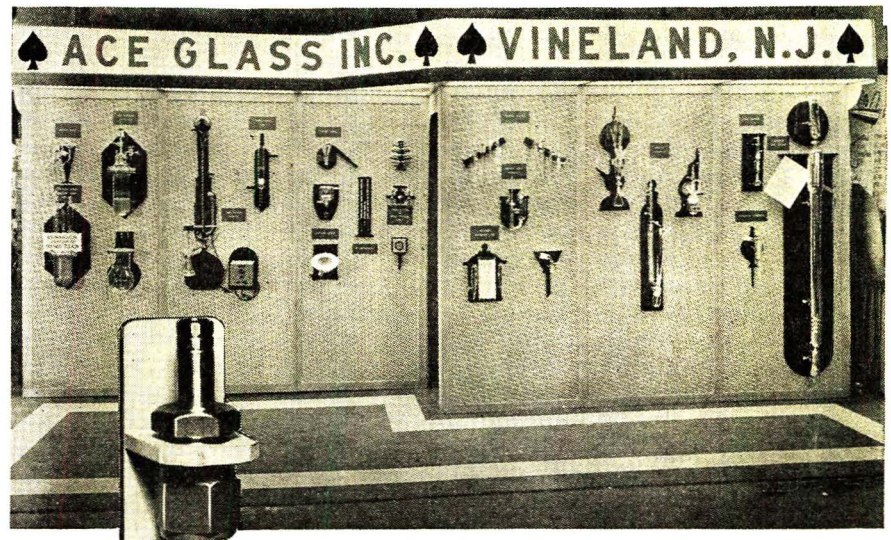
The new instrument is said to permit faster and more accurate initial balancing. The indicating device is an electron-ray eye tube. The unit is contained in a portable hardwood case. **15**

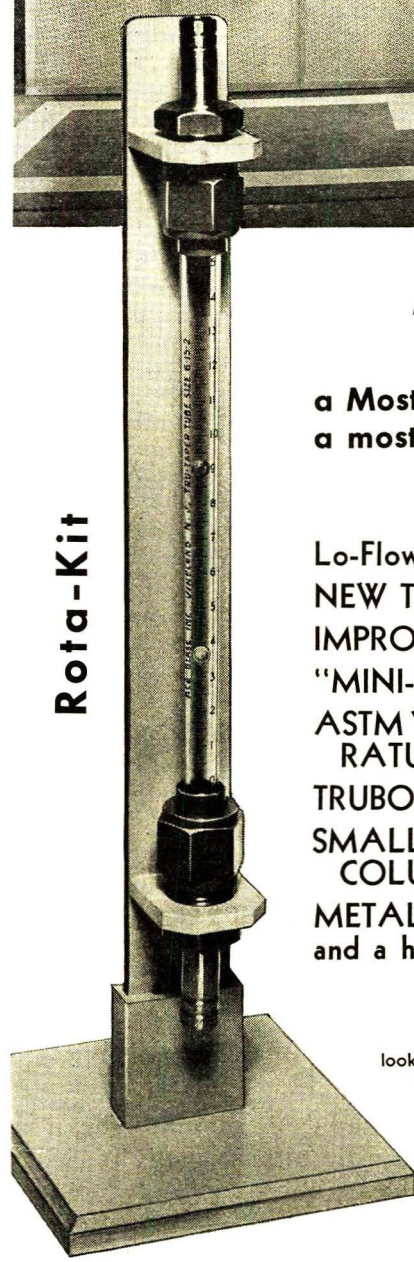
Hydrometer Cylinder

A polyethylene hydrometer cylinder that is nonbreakable and resistant to chemical attack is being produced by American Agile Corp. The cylinder's construction makes it possible to take specific gravity measurements with the cylinder completely filled and the hydrometer at a point where it is easily read. An overflow container catches the displaced liquid, so that valuable materials are not lost nor dangerous liquids spilled.

For further information, see coupon on page 41A

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NEW PRODUCTS, continued

The cylinder is stocked in a size with a 4½-inch base and a 15-inch over-all height that will accommodate most commonly used hydrometers. **16**

Micro-microammeters

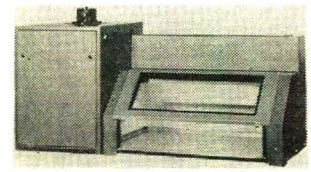
Two new microcurrent instruments for industrial control have been announced by Beckman Instruments, Inc. Both combine high precision and stability, according to the manufacturer, and can be employed to measure, record, and control microcurrents on the order of one millionth of a millionth of an ampere. They can measure the effect of radioactivity on ion chambers or similar sensing devices and can be used for monitoring and industrial control.

Beckman's Model V unit has as its basic unit a vibrating reed modulator which is sealed in a glass envelope and can be replaced as easily as a vacuum tube. The vibrating reed instrument has 13 operating current ranges, including 3×10^{-7} and 3×10^{-13} ampere full scale. Accuracy of 5% or better on any scale is claimed, and readings are independent of line voltage fluctuations from 103 to 107 volts.

For use where input currents are likely to fluctuate, a companion logarithmic scale micro-microammeter has been designed with a wide current range on a single scale. The scale covers six decades from 10^{-7} to 10^{-13} ampere, with each decade graduated in nine subdivisions. The instrument features high resolution, self-calibration, and rapid response, says Beckman. **17**

Sterile Cabinet

A compact, portable, bench model of the Sterilshield dust- and germproof cabinets manufactured by The Baker Co., Inc., is now available for instrument assembly, pharmaceutical, biological, and other work where air-borne contamination is objectionable.



The new Model 12 draws air through an electronic cleaner which removes particles to below 0.01 micron. The clean air is forced into a 40 × 24 inch workspace and maintains a pressure barrier against outside contamination of the area at a 32 × 6 inch opening. This opening permits freedom of movement for the operator without the restriction of arm holes, sleeves, or gloves.

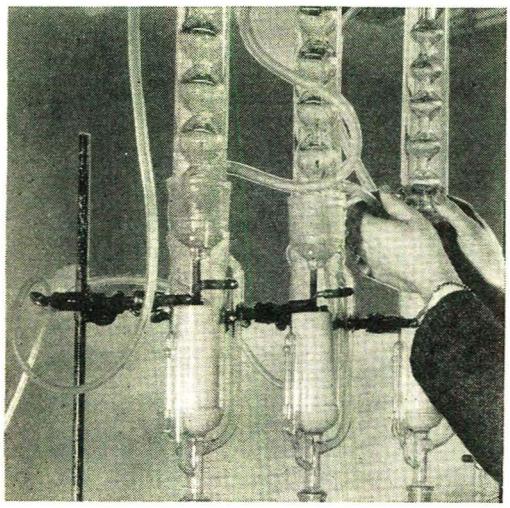
Each cabinet has two fluorescent lamps for illuminating the interior, which is viewed through a plate glass window. Ultraviolet lamps are available as accessory equipment. **18**

Grease Viscometer

A grease pressure viscometer suitable for tests or studies of the flow characteristics of greases under varying conditions of pressure, shear, and temperature has been introduced by Technical Equipment Co. The apparatus meets the specifications of ASTM D-1092 method for the apparent viscosity of lubricating greases.

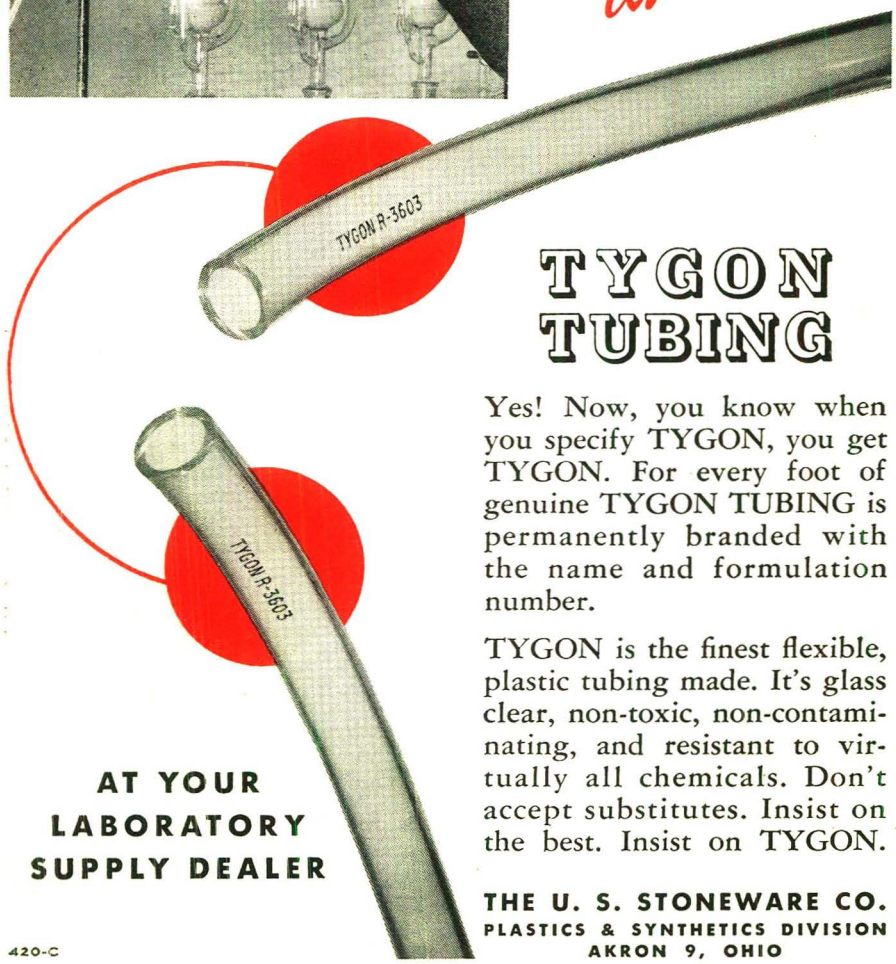
The viscometer's hydraulic system consists of a ¼-hp. motor, a 200:1 speed reducer, a pump, pipe connections, and an oil strainer. Four pressure gages are provided with ranges of 0 to 50, 0 to 100, 0 to 500, and 0 to 2000 pounds per square inch. The viscometer itself is made up of three grease chambers, each with a piston, two end caps, a union connection, and a set of eight interchangeable capillaries. These capillaries have a 40:1 ratio of length to radius. They are made of stainless steel seamless tubing and are housed in

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MANUFACTURERS' LITERATURE

holders having a copper gasket for leakproof attachment to the grease chamber. **19**

MANUFACTURERS' LITERATURE

Electron Microscope. A 12-page booklet describes and illustrates a table model electron microscope and its applications. Radio Corp. of America (*Type EMT*). **20**

Reflectometer. Folder of 4 pages describes an automatic null balance type instrument for measuring reflectance, color, and, with attachments, gloss. Gardner Laboratory, Inc. (*Bull. 132*). **21**

Radiochemicals. Two-page price list of biosynthesized yeast derivatives labeled with sulfur-35 or uniformly with carbon-14. Schwarz Laboratories, Inc. **22**

Fraction Collectors. An 8-page bulletin describes and pictures fraction collection apparatus, including a photoelectric drop counting unit. Technicon Chromatography Corp. **23**

Ultrasonic Equipment. Brochure of 8 pages discusses ultrasonic equipment and its use for nondestructive testing, inspection, and control. Sperry Products, Inc. (*Bull. 50–110*). **24**

Petroleum Testing Apparatus. Three-page price list of apparatus for testing petroleum products in accordance with ASTM and Federal specifications. Technical Equipment Co. (*Price List 53-A*). **25**

Analog Computing Devices. A revised catalog of 8 pages discusses and describes electronic analog computing devices and components. George A. Philbrick Researches, Inc. **26**

Color Difference Meter. Four-page leaflet presents information about an instrument that measures color automatically on three revolving scales to give color difference. Gardner Laboratory, Inc. (*Bull. 144*). **27**

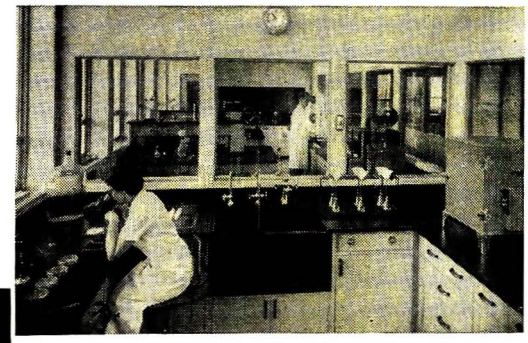
Phloroglucinol. A 6-page reprint from the "Encyclopedia of Chemical Technology" covers physical and chemical properties, occurrence and manufacture, specifications and standards, health and safety considerations, uses, derivatives, and a bibliography for phloroglucinol. Ringwood Chemical Corp. **28**

Gas Analysis Apparatus. A 48-page catalog lists and describes equipment and accessories for gas analysis, presents information on selection, and briefly outlines analytical methods. Burrell Corp. (*Cat. 81*). **29**

For further information, see coupon on page 41 A

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ANNOUNCEMENT

Chemische Fabrik Uetikon of Uetikon, Switzerland, takes pleasure in announcing the appointment of HAGAN CORPORATION as its agent in the United States for the licensing of Uetikon's Schwarzenbach patents Nos. 2,583,890 and 2,583,891. These patents cover revolutionary methods for the quantitative determination of metallic ions with organic chelating agents. Of particular interest is the determination of hardness in water, already widely known. Additional applications of these methods, developed by Dr. Gerold Schwarzenbach of the University of Zurich, are constantly being made.

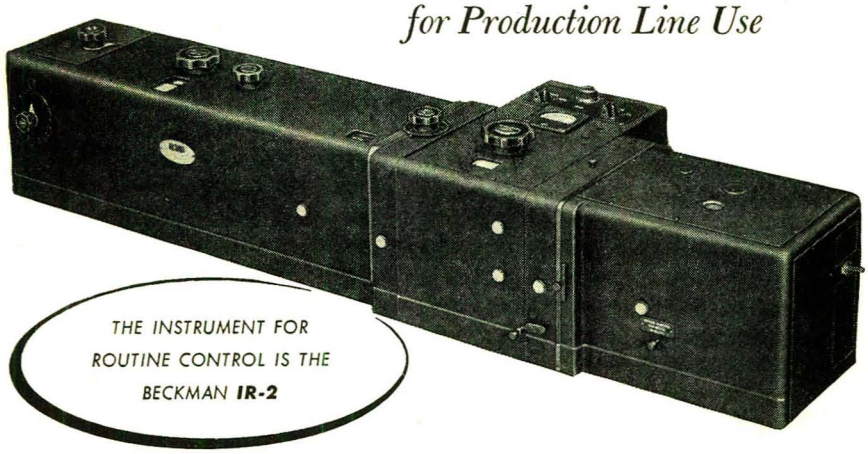
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This instrument will operate from one year to the next with little or no maintenance — even under adverse conditions. Where high humidity, extreme contrasts in temperature, and mechanical shocks have caused other instruments of its type to fail, the Beckman IR-2 has stayed on the job.

For further information, write for Data File 92-15

Beckman *division*

BECKMAN INSTRUMENTS, INC.
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LITERATURE, continued

Heating Equipment. Electric ovens, furnaces, glass annealing ovens, utility water baths, humidity cabinets, and incubators are included in a 40-page catalog of equipment for laboratories, pilot plants, and production. Blue M Electric Co. **30**

Thermal Conductivity Units. A 4-page folder describes and gives specifications for thermal conductivity sensing cells for use in building gas analysis apparatus. Gow-Mac Instrument Co. (*Bull. TC-953*). **31**

Radioisotopes. Development, application, and instrumentation for carbon-14 labeled compounds are described in an 11-page bulletin, "Fisher Radioactive Reagents." Fisher Scientific Co. **32**

Intermediates. Brochure containing 38 pages gives specifications and other information on intermediates for dyestuffs, colors, insecticides, and pharmaceuticals, as well as other products manufactured in Britain by Hickson & Welch, Ltd. (*Brochure 80a*). **33**

ASTM Research. Reprint of 22 pages summarizes research activities, as of May 1953, of the various technical committees of the American Society for Testing Materials. **34**

Spectrochemical Calculator. A 4-page bulletin contains information on the Jaco Fan Scale Calculator, a slide rule type device that quickly provides a continuous check on gamma and eliminates the need for actually plotting the emulsion characteristic curve. Results are read directly in terms of intensity ratio or logarithm of intensity ratio. Jarrell-Ash Co. **35**

Strain Gages. A 12-page price list of strain gages, instruments, and accessories tabulates specifications for 105 types and sizes of gages and presents information on selection and cements. Baldwin-Lima-Hamilton Corp. **36**

Viscosity Determination. A 2-page sheet lists and describes 16 reprints on viscosity determination and control and related subjects that are available from Brookfield Engineering Laboratories, Inc. **37**

Industrial Chemicals. Leaflet of 4 pages gives physical properties and uses of industrial products—as well as market development chemicals available in experimental quantities—produced by Commercial Solvents Corp. **38**

Fine Chemicals. Price lists of pure amino acids and fine chemicals available

For further information, see coupon on page 41 A

LITERATURE, continued

for laboratory and biochemical use from Schwarz Laboratories, Inc. **39**

Organic Chemicals. Supplement of 8 pages lists 47 additions—as well as price changes and removals—in the catalog of organic chemicals available from Distillation Products Industries (*Second Supplement, List 38*). **40**

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Silicones. New silicone products and applications are described in a 2-page company publication put out by Dow Corning Corp. (*Silicone News*). **48**

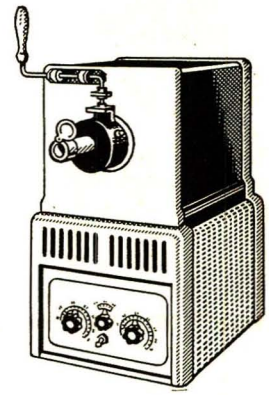
Distilled Water Systems. Valves, fittings, and tubing lined with pure block tin and their use in distilled water systems are described in a bulletin of 12 pages. Autoclave Engineers Sales Corp. (*Cat. 853*). **49**

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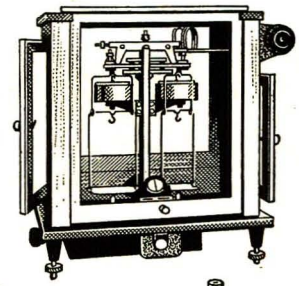
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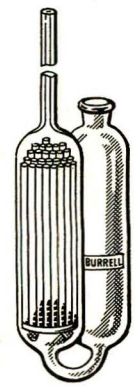
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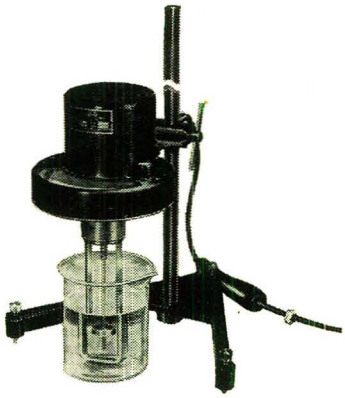
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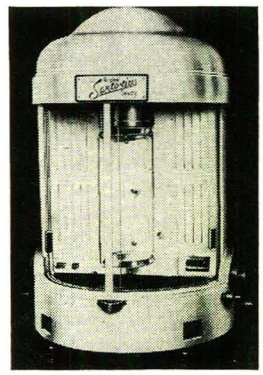
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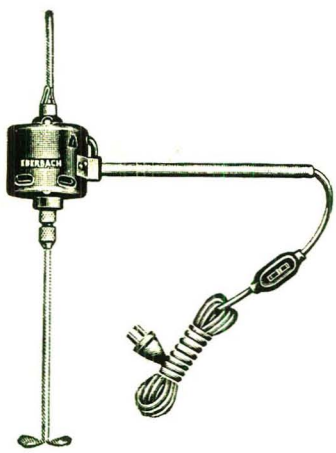


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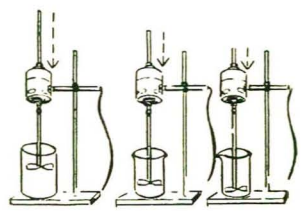
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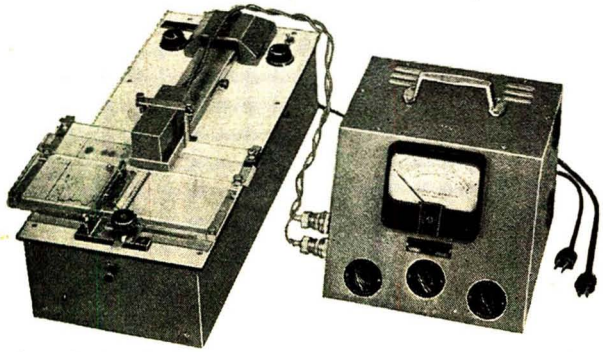
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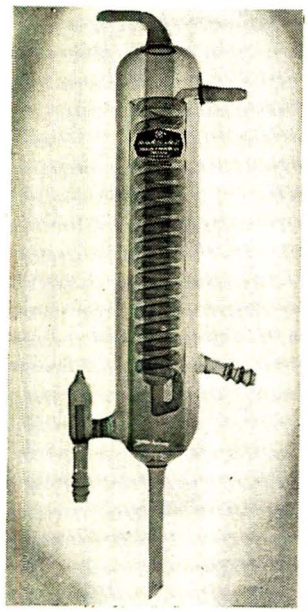
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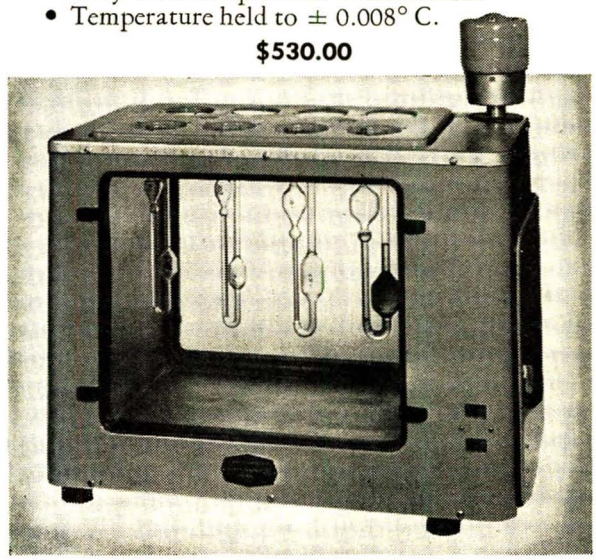
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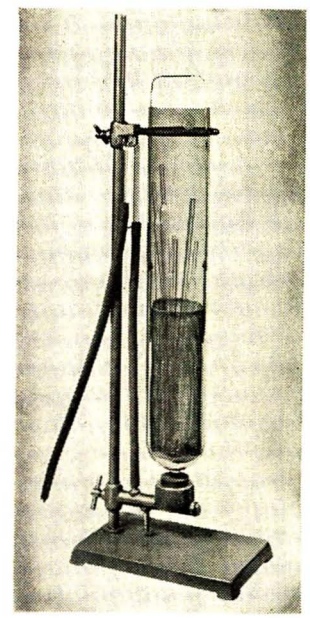
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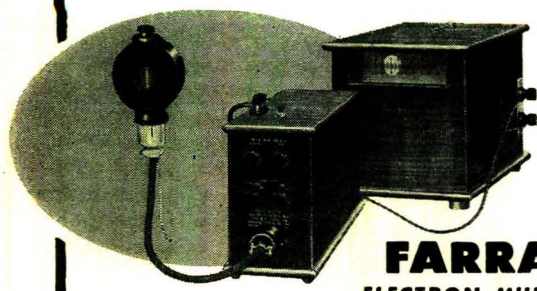
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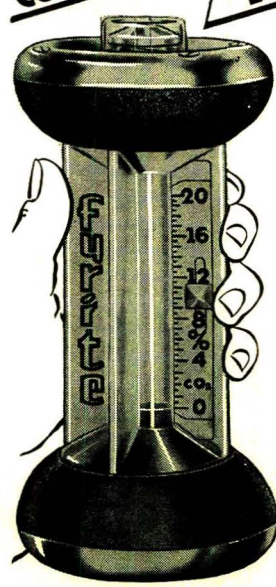
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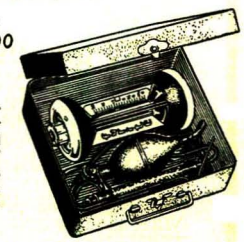
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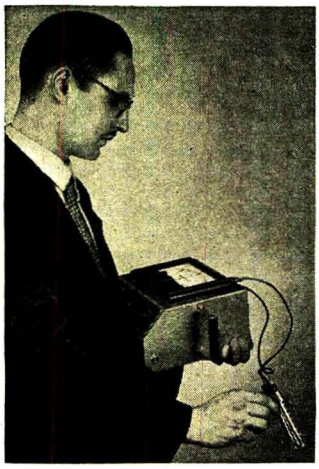
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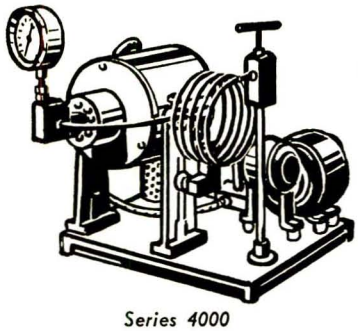
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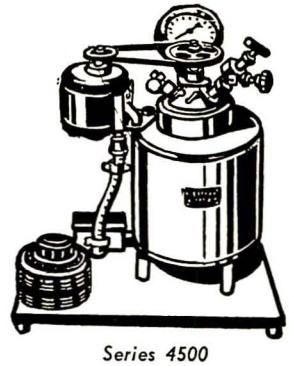
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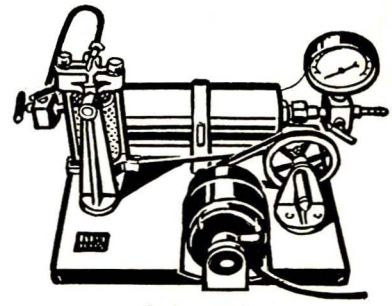
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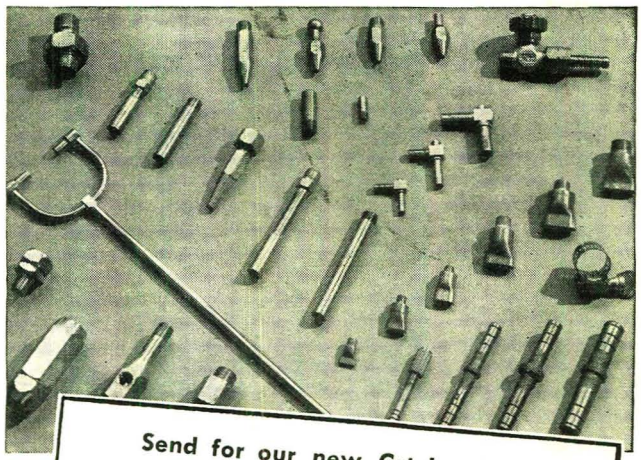
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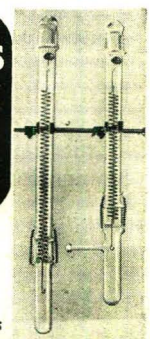
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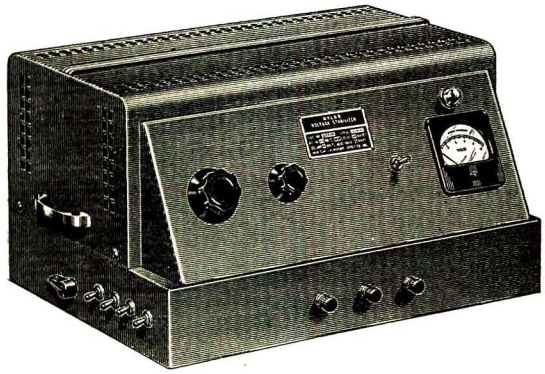
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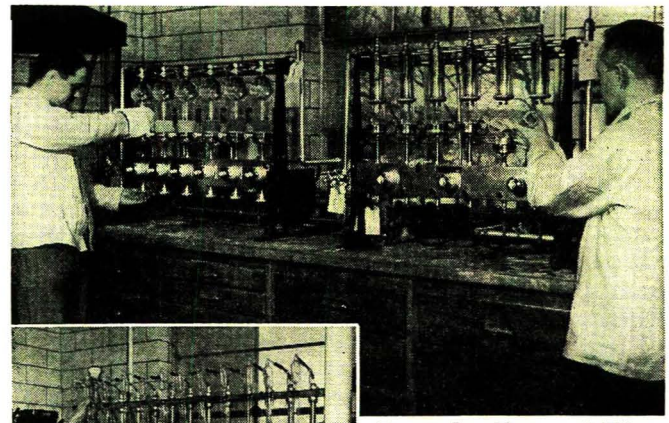
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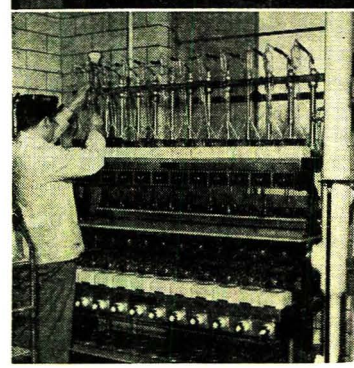
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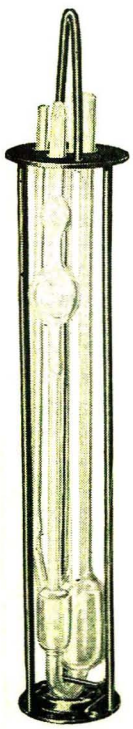
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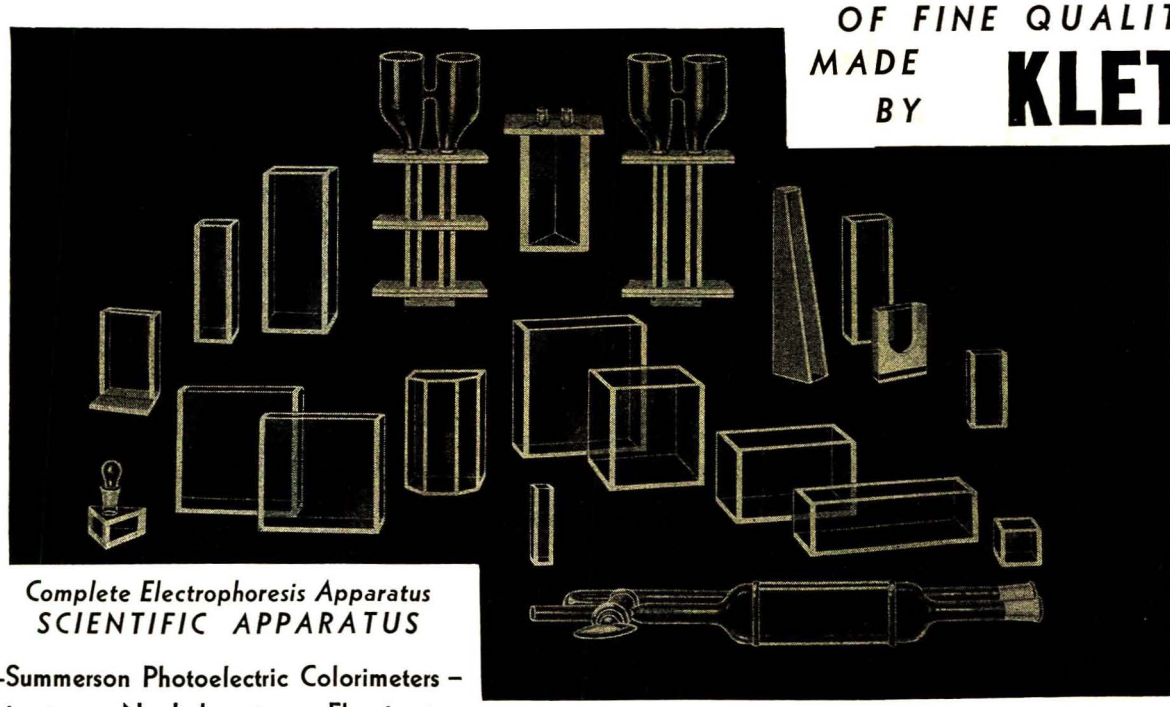
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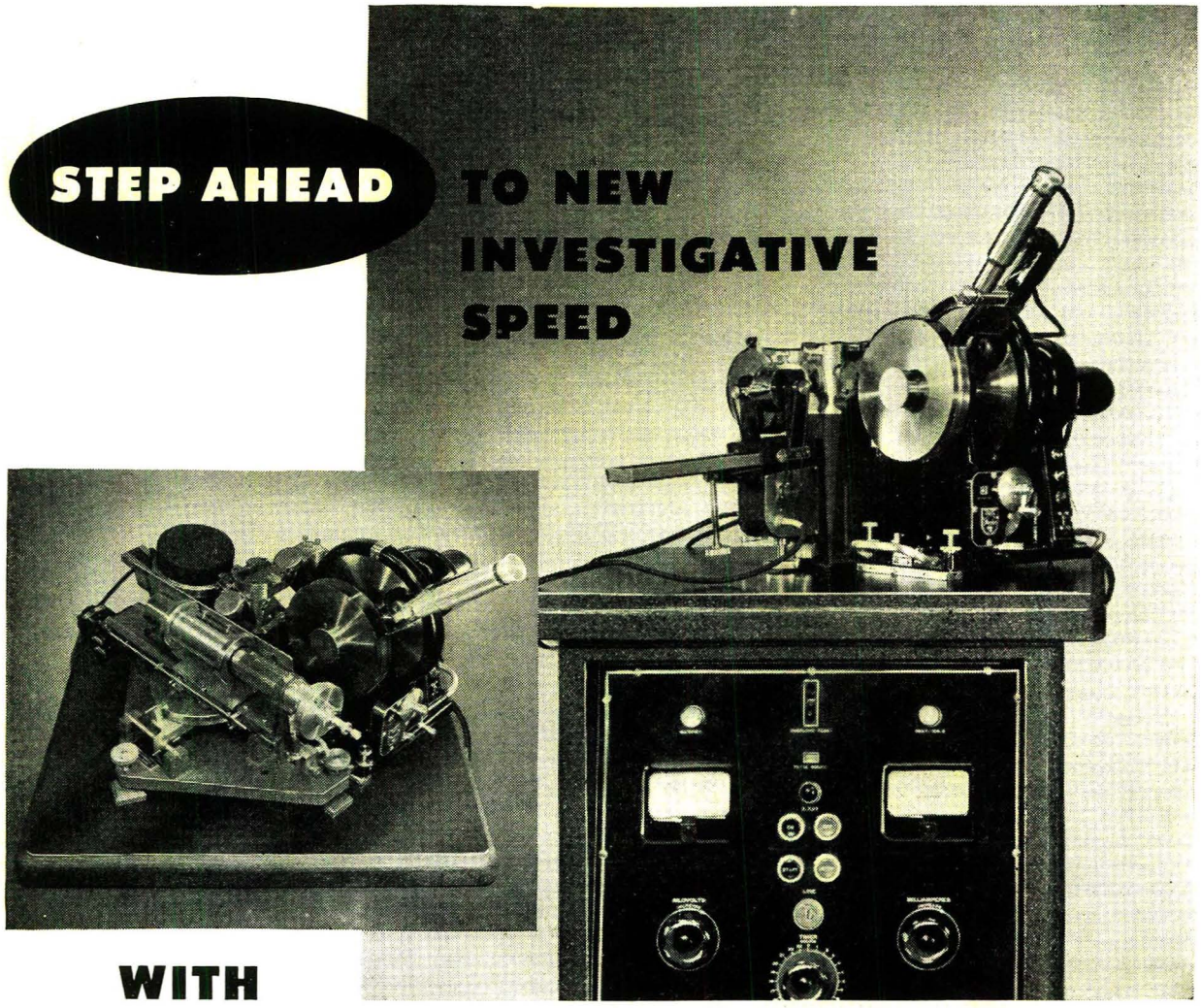
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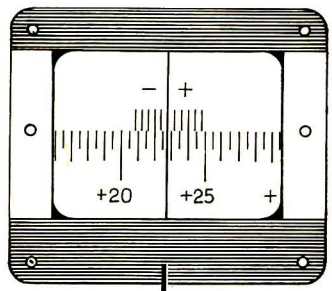
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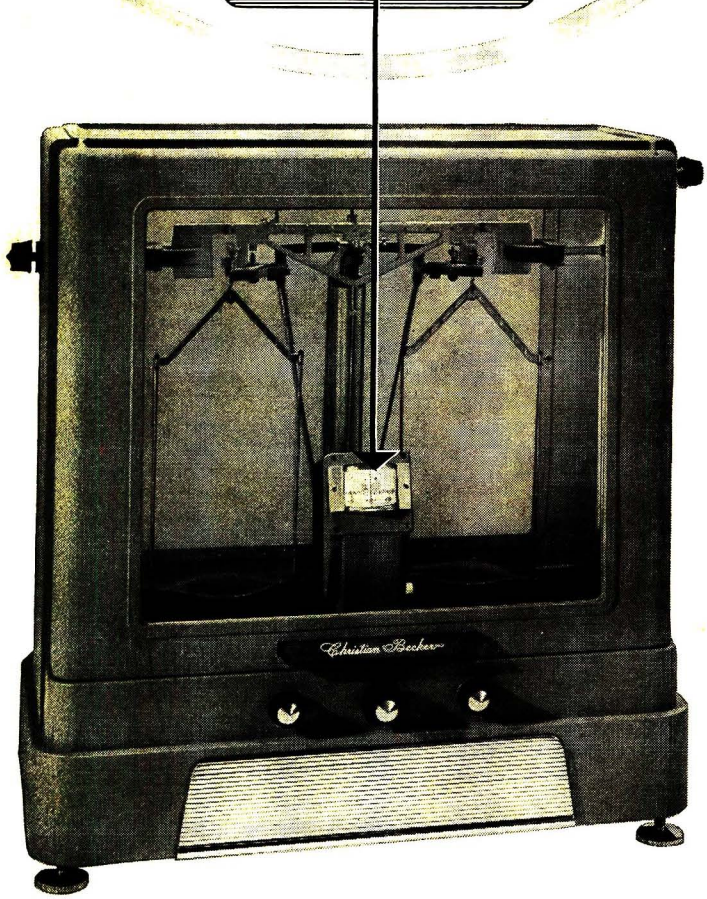
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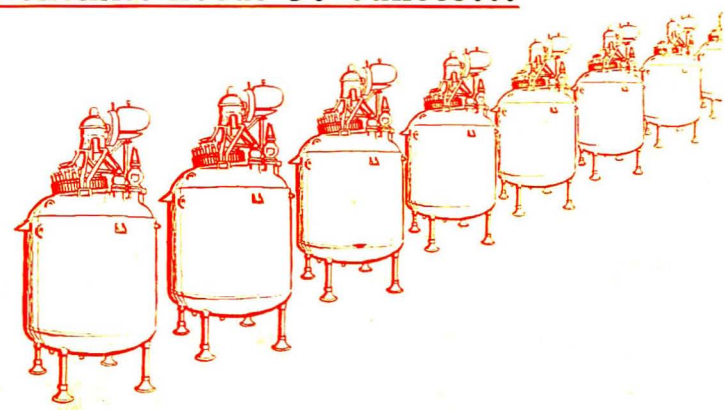
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